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FUNCTIONALITY DETERMINATION OF BINDER PREPOLYMERS

FINAL REPORT

OCTOBER 1, 1966 - SEPTEMBER 30, 1968

Prepared For

**Air Force Rocket Propulsion Laboratory
Research and Technology Division
Air Force Systems Command
Edwards, California**

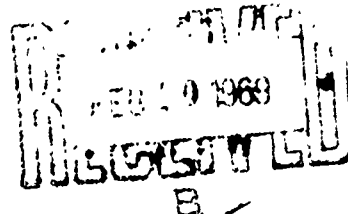
By

**A. H. Muenker and B. E. Hudson
Esso Research and Engineering Company
Linden, New Jersey**

Contract No. F04611-67-C-0012

Esso Report No. GR-8-FBP-68

Esso Project 8110



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FOREWORD

This report describes studies aimed at the development of accurate and reasonably fast test procedures to determine the functionality and functionality distribution of prepolymers currently under development under Air Force sponsorship. This is the Final Report of this investigation. The research was carried out for the Air Force under Contract No. FO4611-67-C-0012 and the program was administered by Lt. Ray Foscante, and Mr. Robert Corley, Air Force Flight Test Center, Edwards Air Force Base, California. The work reported was done in the Government Research Laboratory of the Esso Research and Engineering Company, Linden, New Jersey. Research was carried out during the period October 1, 1966 to September 30, 1968.

The following technical personnel carried out the research: A. H. Muenker (Project Leader) and B. E. Hudson (Principal Investigator). Other technical personnel were assigned briefly for particular problems. The project was under the supervision of Dr. M. S. Cohen, Manager, Chemical Research Programs.

Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

W. H. Ebelke, Colonel, USAF
Chief, Propellant Division

ABSTRACT

This is the final report describing research aimed at the development of accurate and reasonably fast test procedures to determine the functionality and functionality distribution of prepolymers currently of interest to the Air Force. Research was carried out under Contract No. F04611-67-C-002 during the period October 1, 1966 to September 30, 1968. The effect of solute concentration, solvent type and temperature on number average molecular weight measurements by VPO was studied for a series of binder prepolymers. It was concluded that molecular weight measurements of a given polymer in different solvents give identical molecular weights when extrapolated to infinite dilution, although measurements at finite concentrations in different solvents may give widely varying results. A number of micro-methods were developed which can accurately determine the equivalent weight of hydroxy- and carboxy-functional prepolymers on a 50 to 100 mg sample size. A method was also developed to determine the functionality distribution of binder prepolymers. The method is based on the adsorption of prepolymer on activated silica gel and subsequent selective desorption by stepwise elution using solvent mixtures of progressively greater elution power. The following eight prepolymers were studied on this program: OH-Telagen-S, COOH-Telagen-S, P-BEP, 3M's hydroxy-functional perfluoroalkylene oxide prepolymer, COOH-Polyisobutylene, Thiokol's CNR-Nitroso Terpolymer, COOH-Butarez and Sinclair's Poly B-D. Typical prepolymer samples contain from 0-7% nonfunctional polymer, and 16 to 33% monofunctional polymer.

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I. INTRODUCTION

The problem of making high quality binders with reproducible physical properties depends upon the synthesis of prepolymers with reproducible molecular weight, equivalent weight, and distribution of these qualities. Properties such as viscosity of the fine solids-loaded mix and the strength and elongation of the cured propellant are greatly affected by molecular weight and its distribution as well as by the functionality of the polymer. The functionality of a prepolymer which is defined as the ratio of molecular weight to equivalent weight is probably the most important single parameter which determines the nature of the crosslinked polymer network. It requires accurate knowledge of both number average molecular weight and equivalent weight.

Ideally, a suitable prepolymer for propellant binder applications has terminal functionality (OH or COOH). Such a prepolymer has theoretically a functionality of 2.0. Because of uncontrolled chain termination reactions during the prepolymer synthesis, however, not all polymer chains have the desired functional end group. As a result prepolymers generally have a distribution of functionalities, including nonfunctional, monofunctional and the desired difunctional prepolymer. Prepolymers which are prepared by co- or terpolymerization may contain functional groups along the chain rather than terminal functional groups. These prepolymers may have a functionality distribution which includes polymer components having more than two functional groups per polymer chain ($f \geq 3$).

Theoretical considerations predict that monofunctional prepolymer components will seriously affect the mechanical properties of the propellant since monofunctional polymer chains will act as chain terminators during the cure process and hence interfere with the formation of a large polymer network needed to impart good mechanical properties to the propellant. The ability to determine the functionality distribution of prepolymers and to separate prepolymers into non-, mono- and difunctional prepolymers is a prerequisite in studying the effect of functionality distribution on binder and propellant mechanical properties.

This program was therefore concerned with examining and refining available test methods and were required to develop new methods for the characterization of vital prepolymer parameters.

II. OBJECTIVE

The objective of this program is to develop accurate and reasonably fast test procedures to determine the functionality and functionality distribution of prepolymers currently under development under Air Force sponsorship. The specific prepolymers to be studied initially were:

- (1) OH-Telagen-S, a hydrogenated, hydroxy-terminated polybutadiene, being developed by the General Tire and Rubber Company under Contract AF04(611)-10386.
- (2) COOH-Telagen-S, a hydrogenated carboxyl-terminated polybutadiene, also being developed by the General Tire and Rubber Company.
- (3) The energetic binder, P-BEP, being developed by Shell under Contract AF04(611)-8168.
- (4) The high density, high temperature binder being developed by 3M under Contract AF04(611)-11200.

In addition to the above polymers, a number of other prepolymers were characterized under this program. These include Enjay's COOH-terminated Polyisobutylene, (EMD-590), Thiokol's CNR-Nitroso Terpolymer, Phillips' COOH-terminated Butarez, and Sinclair's Poly B-D, a hydroxy-functional polybutadiene.

III. SUMMARY

This is the final report describing research aimed at the development of accurate and reasonably fast test procedures to determine the functionality and functionality distribution of prepolymers currently of interest to the Air Force.

Research discussed in this report was carried out under Contract No. F04611-67-C-0012 during the period of October 1, 1966 to September 30, 1968.

This program was concerned with examining and refining available test methods and were required to develop new methods for the characterization of vital prepolymer parameters.

Vapor pressure osmometry was selected as the most suitable method for determining number average molecular weights in the molecular weight range of interest to binder prepolymers ($M_n = 1000-5000$). The effect of test variables such as temperature, solvent type and polymer concentration was investigated for a series of binder prepolymers. It was demonstrated that molecular weight measurements of a given polymer in different solvents give identical molecular weights when extrapolated to infinite dilution, although measurements at finite concentrations in different solvents may give widely varying results.

For the determination of accurate number average molecular weights it is therefore very important that apparent molecular weight measurements be extrapolated to infinite dilution, $[(M_n)_0]$, to eliminate concentration effects. Furthermore, the concentration dependence of molecular weight for a given polymer-solvent-temperature system cannot be predicted and must therefore be determined experimentally for each such system.

A number of micro-scale methods for the determination of equivalent weight of hydroxy- and carboxy-terminated prepolymers have been developed which can accurately measure this prepolymer parameter on 50-100 mg polymer samples. These methods are based on infrared absorption measurements of prepolymer solutions by measuring the intensity of the hydroxyl or carboxyl functional group. In the case of OH-functional prepolymers, a second independent method was developed which is based on the reaction of the prepolymer with p-toluenesulfonyl isocyanate, a very reactive isocyanate.

Most significantly a method was developed which can determine the functionality distribution of binder prepolymers. The method is based on the adsorption of prepolymer on activated silica gel and subsequent selective desorption by stepwise elution using solvent mixtures of progressively greater elution power. This technique can effectively separate prepolymers into non-, mono- and difunctional components. Prepolymers which can be characterized by this technique include OH-terminated, hydrogenated polybutadienes (OH-Telagen-S), COOH-terminated, hydrogenated polybutadienes

(COOH-Telagen-S), and COOH-terminated polyisobutylenes. The method was also applied to Thiokol's CNR-Nitroso terpolymer and 3M's hydroxy-functional perfluoroalkylene oxide prepolymer. These latter two polymers have functionalities in excess of 2.0.

A total of eight prepolymers were characterized on this program. Emphasis was placed on functionality and functionality distribution measurements. Molecular weight distribution measurements were carried out on only a few select prepolymers.

Functionality distribution measurements on OH-Telagen-S, lot 242 AM-184 AH, have shown that this prepolymer contains significant fractions of both non- and monofunctional components. About 5 wt. % of the polymer is nonfunctional and 25 to 30% is monofunctional.

Two samples of the carboxy-functional analogue (COOH-Telagen-S) were also characterized. COOH-Telagen-S, lot 242 AM-151 BH, contained very substantial fractions of non- and monofunctional prepolymer. Our analyses showed about 8% nonfunctional and 30% monofunctional components. A second sample, lot 242 AM-194 BH, contained considerably less non- and monofunctional components than lot 151 BH. Functionality distribution measurements yielded 2.5% nonfunctional and about 15% monofunctional prepolymers.

Preliminary studies were carried out to explore the possibility of separating non- and monofunctional components from the desired difunctional material by converting the carboxylic acid groups of the polymer to the corresponding potassium salts and subsequently extracting preferentially the dipotassium salts with water. Although polymer of high functionality is preferentially extracted, the method is not selective enough to permit quantitative separation of difunctional prepolymer from the non- and monofunctional components.

The functionality distribution method developed for the Telagen-S prepolymer was also found to be applicable to COOH-terminated polyisobutylene, EMD-59. Fractionation on activated silica gel showed that the particular sample available for characterization contained less than 2% nonfunctional and about 17% monofunctional prepolymer.

Three different lots of P-BEP, Shell's energetic, hydroxy-functional prepolymer, were characterized. The average overall functionality of these lots varied from 1.81 to 2.0 based on equivalent weight measurements by reacting P-BEP with toluenesulfonyl isocyanate. Attempts to determine the functionality distribution of P-BEP by selective desorption from silica gel failed because of decomposition of the P-BEP on the adsorbent. Other adsorbents such as alumina, charcoal, florisil, offered no advantage over silica gel. Molecular weight distribution measurements on one of the P-BEP lots showed that low functionality is associated with low molecular weight. About 20 wt. % of the polymer had a molecular weight of 1500 or below and a functionality of $f \leq 1$. Separation of this low molecular weight, low functional component should improve the mechanical properties of the cured P-BEP binder.

A sample of Thiokol's CNR-nitroso prepolymer containing carboxy-functional groups along the chain was also characterized with respect to functionality and functionality distribution. Because of solubility limitations and the highly acidic character of the perfluoro acid groups, the technique previously developed for the determination of functionality distribution was not directly applicable and had to be modified.

As expected functionality was strongly dependent on molecular weight. Lot A001-4D was found to have the following functionality distribution: 10% nonfunctional, 10-11% monofunctional, 20% difunctional, 17-18% tri- and tetrafunctional, 20-21% pentafunctional and the remaining 20% which could not be desorbed is assumed to have a functionality in excess of 5.0.

3M's hydroxy-functional perfluoroalkylene oxide prepolymer also was found to have a wide distribution of functionalities, extending from 0 to at least 4. In fact the bulk of the polymer (>65%) has a functionality of 3 or above. The approximate functionality distribution was as follows:
< 1% nonfunctional, 7% monofunctional, 17% difunctional, 24% trifunctional, and 41% tetrafunctional. The remaining 10% are believed to have a functionality of 4 or above.

The functionality distribution of COOH-Butarez, type II, lot 2285, could not be clearly defined. Unsaturation in the polybutadiene backbone is believed to interfere with the fractionation by functionality. Our data indicate, however, that this lot contained 10 to 15% of non- and monofunctional prepolymer.

IV. TECHNICAL PROGRESS

Under Contract FO4611-67-C-0012, Esso Research and Engineering Company carried out a program to develop accurate and reasonably fast test procedures to determine the functionality and functionality distribution of prepolymers currently of interest to the Air Force as propellant binders. Research discussed in this report was carried out during the period of October 1, 1966 to September 30, 1968.

This program was concerned with examining and refining available test methods to develop superior methods for the complete characterization of prepolymers.

In Section IV-A we have discussed briefly such prepolymer parameters as number average molecular weight, functionality, functionality distribution and molecular weight distribution. In the subsequent Section IV-B, the analytical methods discussed in IV-A have been applied to a number of hydroxy- and carboxy-functional prepolymers.

A. CHARACTERIZATION PARAMETERS OF
FUNCTIONALLY-TERMINATED PREPOLYMERS

1. NUMBER AVERAGE MOLECULAR
WEIGHT MEASUREMENTS

The accuracy with which the functionality of a given prepolymer can be measured depends on the accuracy with which number average molecular weight and equivalent weight can be measured. From an examination of available test methods and their limitations for number average molecular weight measurements, we selected vapor pressure osmometry (VPO) as the most suitable method for the low molecular weight range (1000-5000) of interest in connection with binder prepolymers. Vapor pressure osmometry (VPO) is a thermoelectric differential vapor pressure technique for determining number average molecular weight (M_n) of polymers of low or moderate molecular weight. The thermoelectric method has significant advantages in speed and in small sample size. The basis of the thermoelectric method is the measurement of the small temperature difference resulting from a differential mass transfer between droplets of pure solvent and polymer solution maintained in an atmosphere of solvent vapor. A detailed discussion of this method is given in Appendix A-1. Other molecular weight methods were considered at the start of this program but were subsequently dropped in favor of the VPO method. These methods are also discussed in Appendix A-1.

Our experience has shown that the reproducibility of the VPO method is generally within 1-3%. Most of our number average molecular weight measurements were made with a Mechrolab Model 302 Vapor Pressure Osmometer. During the latter part of the program the Hitachi Perkin-Elmer Molecular Weight Apparatus became available. Two attractive features of this new instrument are the apparent ease with which one can change from one solvent to another, and the fact that the temperature control is continuously variable. In searching for suitable solvent/temperature combinations applicable to new polymer systems, these two features promise considerable time savings. A third feature, which may prove to be largely an operating convenience, is the provision for direct connection to a strip-chart millivolt recorder. This provides a continuous record vs. time of approach to equilibrium and reproducibility of measurement. Should a drift occur, the rate of drift can also be recorded.

Based on our initial operation and testing of the Model 115 Hitachi Perkin-Elmer Molecular Weight Apparatus, we could not substantiate claims of greater sensitivity.

Low functionalities of binders have traditionally been blamed on errors in the number average molecular weight measurement. It is true that molecular weight measurements can be seriously lowered by the presence of low molecular weight impurities, notably residual solvent and anti-oxidants. If possible, molecular weight measurements should therefore

be carried out after all residual solvent has been removed and before anti-oxidant is added to the prepolymer. If the residual solvent is the same as that used in the molecular weight determination, the effect will be merely one of dilution.

There are other factors, though, which must be considered:

1. There is the possibility of polymer-polymer association which may lead to an apparently higher molecular weight.
2. And there is the general phenomenon of polymer-solvent interaction.

In our molecular weight measurements, we have dealt with the effect of (a) solute concentration, (b) solvent type and (c) temperature on number average molecular weight measurements by VPO for a series of binder prepolymers. Based on our studies we have concluded that molecular weight measurements of a given polymer in different solvents give identical molecular weights when extrapolated to infinite dilution, although measurements at finite concentrations in different solvents may give widely varying results. For the determination of accurate number average molecular weights it is therefore important that apparent molecular weight measurements are extrapolated to infinite dilution $[\bar{M}_n]_0$ to eliminate concentration effects. The concentration dependence of molecular weight for a given polymer-solvent-temperature system cannot be predicted and must therefore be determined experimentally for each such system.

In attempts to improve the precision of the VPO method, we have adopted an innovation in the instrument operating technique. Also, mathematical aspects were explored and a new method of linearly treating VPO calibrations and read-back data was adopted. These innovations are discussed below.

Innovation in VPO Instrument Operating Technique

In normal operation of the Mechro-Lab vapor pressure osmometer, the decade dials are set at 00.00 and the bridge is brought to electrical balance by means of the "balance" control when droplets of pure solvent are on both thermistors.

Our rather simple innovation consists of locking the "balance" control at a fixed position so that solvent vs. solvent balance is attained at a decade setting of approximately 10 or perhaps 25 ohms. In this way a definite resistance value, R_{ss} , is obtained in the solvent vs. solvent test. A different reading, R_{soln} , is observed when the solution droplet is put in place. ΔR is then obtained as the difference, $R_{soln} - R_{ss}$, for use in subsequent computations.

The modified operating technique has several advantages over the customary procedure. First, it provides a quantitative basis for checking cleanliness of all syringes prior to subsequent analysis. Secondly, accumulated R_{ss} readings lead to a statistical value to be used in computing the ΔR values when readings (R_{soln}) are taken on a series of solutions. Thirdly, through providing a means for recording the probe balance point (R_{ss}) over a long period of time, this operating method provides a basis for early detection of functional deterioration of the thermistor beads.

Coincidentally, this innovation in operation of a two-thermistor VPO instrument partially approximates a single-thermistor arrangement which is featured in a new VPO instrument manufactured by Hitachi/Perkin-Elmer and recently introduced commercially in the USA.

Linearization of Calibration

In the calibration of a vapor pressure osmometer, the correlation of the resistance change, ΔR , with the concentration of the dissolved calibrating substance is nearly always non-linear. A significant part of this non-linearity is inherent in the thermodynamics of the quasi-steady state non-equilibrium processes on which the method is based. The essential physical basis for the VPO method is outlined in Appendix A-1. In a recent publication, (1) Adicoff and Murbach show that for a given solvent the primary calibration constant is independent of the calibrant used, but that the degree of curvature is dependent upon and characteristic of the solute-solvent combination. Further non-linearity arises when it is necessary to prepare solutions and express concentrations on the basis of solution weight (grams or mol/Kg. soln.) rather than on a solution volume basis.

The solid curve of Figure 1 represents, in linear coordinates, the ΔR vs. concentration (mol/Kg. soln.) response obtained with tetracosane ($n\text{-C}_{24}\text{H}_{50}$) calibrant and 1,2-dichloroethane solvent at 37°C . The practical problem of drawing a curved line accurately is perhaps obvious. Difficulties become compounded in the region of low ΔR values where precision of measurement is limiting in both calibration and analysis. The so-called intercept method in which $\Delta R/C$ is plotted against C and extrapolated to $C = 0$ to obtain an initial slope, $(\Delta R/C)_0$, is also illustrated in Figure 1. The several dashed straight lines represent estimates of initial slopes and emphasize both the uncertainty of accurately determining $(\Delta R/C)_0$, and its rather unreal significance at moderate to high concentrations. Use of the intercept method effectively concentrates non-linearity from all sources into a final exaggerated dependence of apparent molecular weight upon concentration of the solute.

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- (1) Adicoff, A. and Murbach, W. J., Anal. Chem., Vol. 39, 302 (1967).
See also Report NOTS TP 4247, Naval Ordnance Test Station, China Lake, California, March 1967.

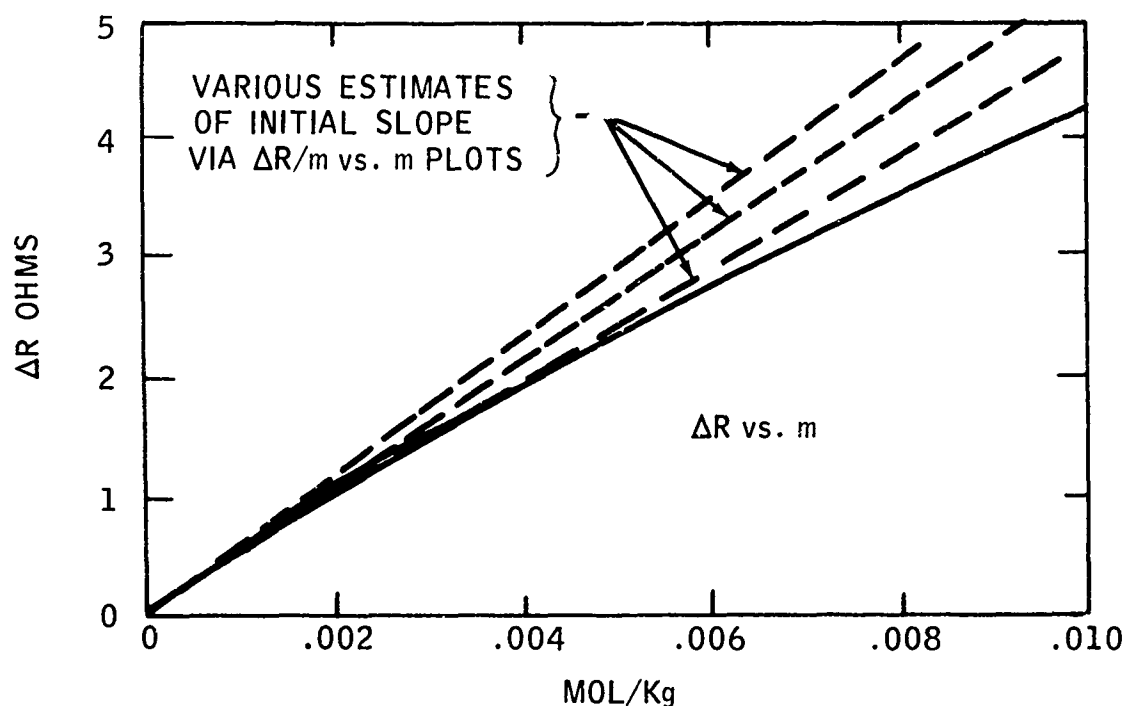


Figure 1. VPO calibration, tetracosane ($n\text{-C}_{24}\text{H}_{50}$) in 1,2-dichloroethane solvent, 37°C , linear coordinates. (Dashed lines represent initial slope estimates)

To overcome difficulties inherent with curvilinear plots and with the intercept method of treating calibration data, a new scheme for plotting calibration data has been explored and adopted. In principle and thus far in practice, $\log \Delta R$ vs. \log concentration (mol/Kg. soln.) yields a straight calibration line over a wide concentration range. This is illustrated (without data points) in Figure 2 for comparison with other types of plots discussed with reference to Figure 1. Figure 59 in Appendix A-1 shows the log vs. log calibration plot on a larger scale, with data points. Linearity over a wide range is confirmed. The plot also suggests that extrapolation into the region of low ΔR values (< 1 ohm) is probably more precise than direct calibration in that region.

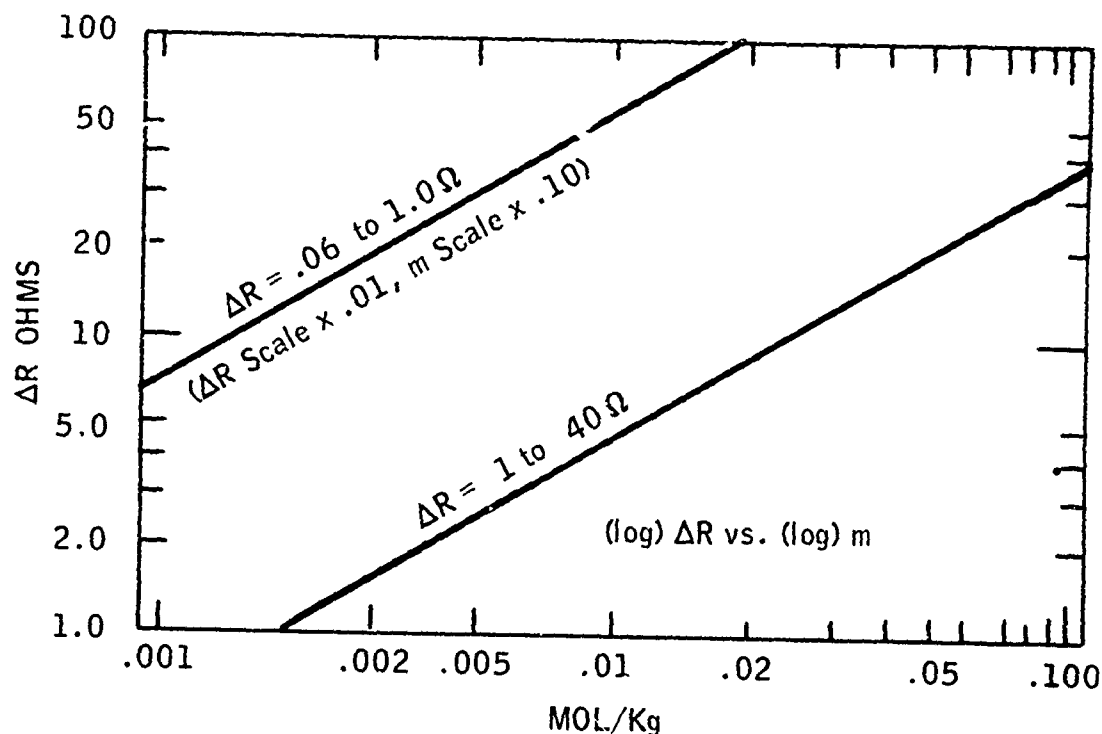


Figure 2. VPO calibration, tetracosane ($n\text{-C}_{24}\text{H}_{50}$) in 1,2-dichloroethane solvent, 37°C , logarithmic scales

The validity of the $\log \Delta R$ vs. \log concentration plot is substantiated by a series of mathematical considerations. An initial assumption that the curvature encountered in VPO calibrations can be fully expressed as a combined first and second order dependence of ΔR on concentration is borne out by reference (1).

A general equation which includes a first and second order dependence of ΔR upon concentration, C , and upon molecular weight, M , may be written:

$$\Delta R = k \cdot \frac{C}{M} - k' \left(\frac{C}{M} \right)^2 \quad (1)$$

where: ΔR = measured resistance increment

C = concentration of solute, typically in grams/kilogram of solution

k = sensitivity factor for the solvent and temperature combination

k' = system non-linearity factor, expressing second order concentration dependence of ΔR upon instrument, solvent and solute combination

An obvious rearrangement is:

$$\Delta R = \frac{kC}{M} \left(1 - k'' \frac{C}{M} \right) ; \text{ where } k'' = k'/k \quad (2)$$

which can be further simplified to:

$$\Delta R = km (1 - k''m) \quad (3)$$

$$\frac{C}{M} = m = \text{mol/Kg.}$$

Since $(1 - a) = e^{-a}$ when a is small:

$$\Delta R = kme^{-k''m} \quad (4)$$

In log form:

$$\log \Delta R = \log km - k'''m \quad (5)$$

$(k''' = k'' \cdot \log \text{ base conversion factor})$

Also:

$$\log \left(\frac{\Delta R}{km} \right) = -k'''m \quad (6)$$

Thus from equations (5) and/or (6) a plot of $\log \Delta R$ vs. $\log m$ will be a straight line deviating from unit slope by a factor proportional to m . This should be a straight line over a wide range since the product $k'''m$ is relatively small.

2. EQUIVALENT WEIGHT MEASUREMENTS

There are a number of wet chemical methods for the determination of equivalent weight of hydroxy- and carboxy-functional prepolymers which are routinely used on prepolymers. In the case of hydroxy-functional prepolymers, the method is based on the reaction of the OH-end group with anhydrides of organic acids which is stoichiometric in the presence of pyridine. For carboxy-functional prepolymers accurate equivalent weight measurements are obtained by potentiometric titration of an MEK solution of the polymer with 0.1 N tetrabutyl ammonium hydroxide in methanol. These conventional methods, however, require relatively large sample sizes (in the order of grams).

When fractionating prepolymers, small fractions of polymer need to be characterized with respect to molecular weight and equivalent weight. There was therefore a need for small-scale equivalent weight methods which can accurately determine the equivalent weight of 50 to 100 mg polymer fractions.

The methods we have used in the case of COOH-functional prepolymers is based on measuring the intensity of the carbonyl absorption band at $5.7 - 5.8 \mu$ in the infrared. A calibration is needed which relates the intensity of the carbonyl absorption band to the molar concentration of the calibrant. In selecting a suitable calibrant, two approaches are feasible: (1) simulate the functional group of the prepolymer by using a carboxylic acid such as stearic acid, as the calibrant; (2) an alternate method is to use the given prepolymer whose equivalent weight has been accurately determined by base titration, as the calibrant.

A plot of carbonyl absorbance with molar concentration using stearic acid and COOH-Telagen-S of known equivalent weight as the calibrant gave the same identical correlation for both polymer and stearic acid.

Tetrahydrofuran was chosen as the solvent so as to prevent polymer-polymer association and to give a linear response of the intensity of the carbonyl absorption band with COOH molar concentration. The equivalent weight determination based on infrared absorption measurements is nondestructive and requires only small polymer samples. In practice, the equivalent weight of a polymer is determined by first determining the carbonyl absorbance of the polymer solution of known concentration and secondly reading from the calibration the molar concentration which corresponds to the particular absorption intensity.

The above method has also been applied to OH-terminated prepolymers by measuring the intensity of the hydroxyl band at 2.72 and 2.82μ . Butanol reference blend in a 25 vol. % ethyl acetate/75% carbon tetrachloride solvent mixture were used to establish a linear calibration. The infrared method which measures the intensity of the hydroxyl or carbonyl band is discussed in detail in Appendix A-2.

The Diborane method is another independent method for the determination of the equivalent weight of hydroxy-functional prepolymers which was investigated on this program. Basically the method involves the reaction of diborane with protonic material and measuring, manometrically, the evolved hydrogen. Equivalent weight data obtained on P-BEP by the Diborane method differed considerably from the data obtained by the infrared absorption technique. It was, therefore, desirable to establish an independent third method for the determination of the equivalent weight of hydroxy-terminated prepolymers, specifically the P-BEP prepolymer. The method we developed is based on the reaction of the hydroxyl group of the prepolymer with p-toluenesulfonyl isocyanate, a very reactive isocyanate. The reaction is carried out in dilute solution at room temperature and is extremely rapid. The isocyanate-hydroxyl reaction is monitored spectrophotometrically (infrared) by measuring the disappearance of the NCO stretching vibration at 4.4 to 4.5 μ . The isocyanate absorbance at zero time is obtained from a calibration plot of the isocyanate. The equivalent weight is calculated from the amount of isocyanate that has reacted with a known amount of prepolymer. The feasibility of this method as an independent accurate, small-scale hydroxyl-equivalent weight method applicable to all hydroxy-functional prepolymers has been confirmed. The method is very reproducible and requires only 50 to 100 mg sample size. A detailed discussion of this method is given in Appendix A-2.

3. FUNCTIONALITY DETERMINATION

Functionality of a prepolymer is defined as the ratio of number-average molecular weight to equivalent weight. Functionality can therefore be calculated from separate measurements of molecular weight and equivalent weight. In addition to this indirect functionality determination, there are two principal methods for the direct determination of functionality. These are the Flory Condensation Polymer Method and the Crosslink Density Method. All of the three methods are subject to limitation as discussed in Appendix A-3. All functionality measurements in this report are based on molecular weight and equivalent weight measurements.

4. FUNCTIONALITY DISTRIBUTION MEASUREMENTS

Prepolymers do not in general have theoretical functionality. The determination of functionality distribution, that is the percentages of non-, mono- and difunctional polymer components is therefore of particular importance, since functionality distribution will affect propellant mechanical properties.

The method we have developed to determine the functionality distribution of binder prepolymers is based on the adsorption of prepolymer on activated silica gel and subsequent selective desorption by stepwise elution using solvent mixtures of progressively greater elution power. This technique can effectively separate prepolymers into non-, mono- and difunctional components. Nonfunctional polymer which has no polar groups for adsorption by the silica gel is eluted first from the column. Monofunctional polymer which is adsorbed on the column packing at one end of the polymer chain is eluted next in response to a more polar solvent mixture. Difunctional polymer requires a progressively more polar solvent mixture to be desorbed since it is adsorbed on the silica gel surface at both ends of the polymer chain. Based on the elution profile, individual polymer fractions are appropriately recombined into 3 or more major fractions and analyzed for functionality. Prepolymers which have been characterized by this technique include OH-terminated, hydrogenated polybutadienes (OH-Telagen-S), COOH-terminated, hydrogenated polybutadienes (COOH-Telagen-S), and COOH-terminated polyisobutylenes. Typical prepolymer samples analyzed to date contain from 0-7% nonfunctional polymer, and 16 to 33% monofunctional polymers. The method was also applied to nitroso-terpolymers and 3M's hydroxy-functional perfluoroalkylene oxide prepolymer. These latter two polymers have functionalities in excess of 2.0. Details of the functionality distribution method are discussed in appropriate sections dealing with the characterization of specific prepolymers.

Preliminary fractionation studies have shown that unsaturation in the prepolymer tends to interfere with the separation by functionality. This parameter requires further studies.

The ability to determine the functionality distribution of prepolymers and to separate prepolymers into non-, mono- and difunctional prepolymers is a prerequisite in studying the effect of functionality distribution on binder and propellant mechanical properties. It opens up new areas of binder studies such as the establishment of the relationship between mechanical properties and monofunctional prepolymer content. Such experimental investigations were hitherto inaccessible because of lack of appropriate analytical techniques.

5. MOLECULAR WEIGHT
DISTRIBUTION MEASUREMENTS

Since this program was mainly concerned with the determination of functionality and functionality distribution, molecular weight distribution measurements were not routinely carried out on all prepolymers. Two methods were employed: (1) osmodialysis which capitalizes on one of the limitations of ordinary membrane osmometry, namely the fact that low molecular weight species tend to diffuse through a semipermeable membrane and (2) Gel Permeation Chromatography which is a type of liquid-liquid column chromatography. Both of these methods are discussed in detail in Appendix A-5.

B. CHARACTERIZATION OF SPECIFIC PREPOLYMERS

A total of eight prepolymers were characterized on this program. Emphasis was placed on functionality and functionality distribution measurements. Molecular weight distribution measurements were carried out on only a few select prepolymers. The results of our characterization studies are summarized in the following sections.

1. OH-TELAGEN-S, 242 AM-148 AH

OH-Telagen-S is a hydrogenated, hydroxy-terminated polybutadiene prepared by the General Tire and Rubber Company. All work reported on OH-Telagen-S was done with batch No. 242 AM-148 AH, Lot No. BH-392605.

1.1. Molecular Weight Determination

From the number of methods which have been used for molecular weight determination we selected initially two methods: (1) Vapor pressure osmometry and (2) Osmodialysis. It was realized that osmodialysis is correlative and not absolute as regards molecular weights. Primarily for this reason, the mean or average molecular weight data by osmodialysis should not be used for the calculation of functionality of polymers.

(a) \bar{M}_n by Vapor Pressure Osmometry (VPO)

The vapor pressure osmometry measurements were made initially with a Model 302 vapor pressure osmometer (Mechrolab Inc.) with benzene at 37°C. As pointed out in Section IV A1, the VPO method depends on reproducibly measuring the temperature difference between droplets of solution and solvent deposited on two sensitive thermistors when they are brought into quasi-equilibrium. In practice, this temperature difference is measured as the difference of the resistance (ΔR) of these thermistors. This latter quality is proportional to the temperature difference and can be measured more precisely. We have studied the change in ΔR with time at a series of different polymer concentrations varying from 5.03 to 35.75 g/Kg of solution. In general, a constant value of ΔR was reached after 3-5 minutes. The reproducibility was generally within 1-3%.

Of particular interest is the effect of polymer concentration on the apparent molecular weight. If the polymer solution behaved ideally, the ratio of ΔR to concentration ($\Delta R/C$) should be independent of C . Owing to the large effective size of the polymer molecules in solution and the interactions between them, $\Delta R/C$ increases generally with C with a slope which depends on the interaction between the solvent and the solute. Because of this concentration dependence of $\Delta R/C$, it is necessary to extrapolate the plot of $\Delta R/C$ vs. C to infinite dilution ($C \rightarrow 0$) and from the intercept, $(\Delta R/C)_0$, the number average molecular weight (\bar{M}_n) is calculated. Since $\Delta R/C$ is proportional to $1/\bar{M}_n$, an alternate method involves plotting apparent molecular weight (\bar{M}_n apparent) versus C and determining the intercept at $C=0$. Figures 3 and 4 show the corresponding plots of $\Delta R/C$ and

(\bar{M}_n) apparent versus concentration for Telagen-S. The extrapolated molecular weight $(\bar{M}_n)_0$ was found to be 1950 ± 50 which is somewhat higher than that reported by Aerojet. Aerojet has reported a value of $\bar{M}_n = 1780$ by VPO. It is not known to the writer whether this value is based on $(\Delta R/C)_0$ or represents a measurement at some finite concentration. Figure 4 shows that a measurement at a single concentration of about 25 g of Telagen/Kg of solution (in benzene) would indeed give an apparent molecular weight of 1800.

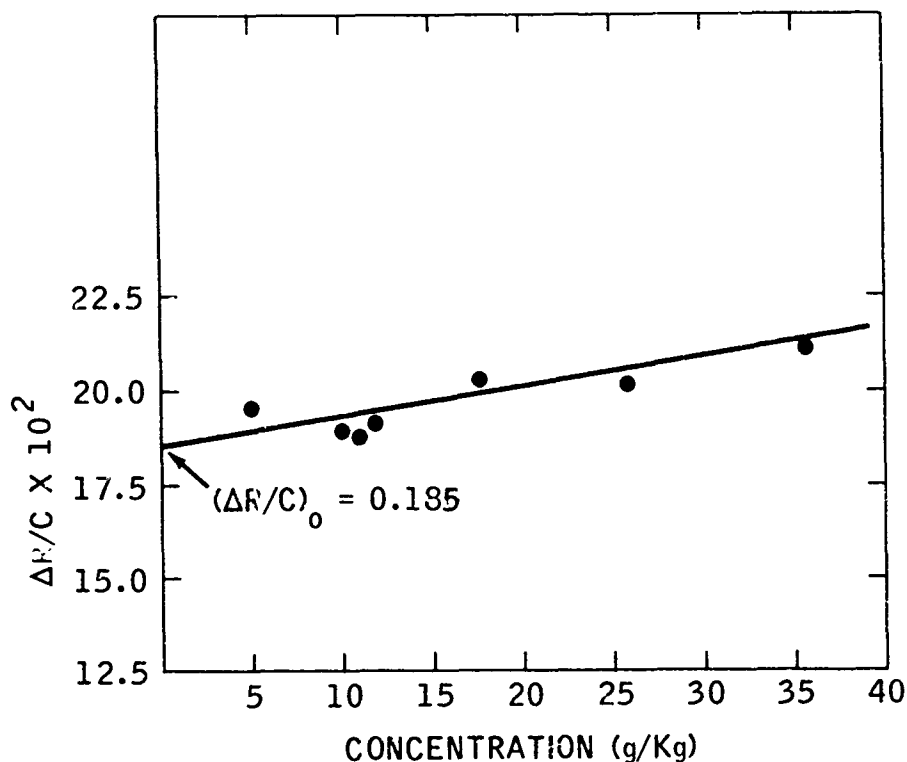


Figure 3. Dependence of $\Delta R/C$ on concentration for OH-Telagen-S, 242 AM-148 AH in benzene at 37°C. $(\Delta R/C)_0 = 0.185$

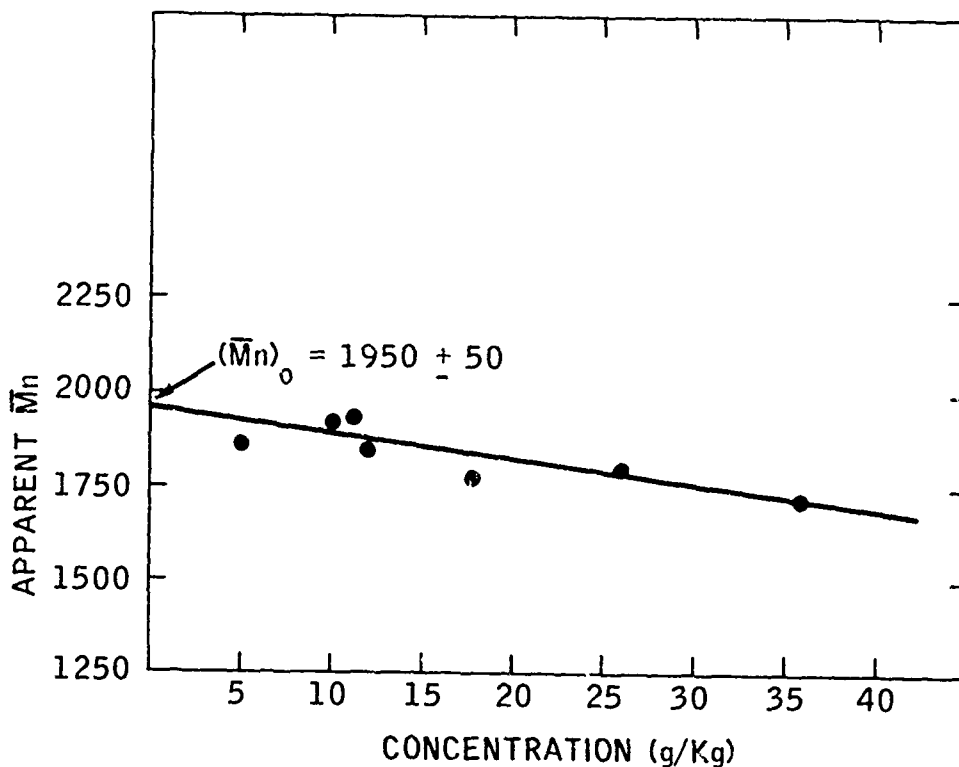


Figure 4. Dependence of apparent molecular weight (\bar{M}_n) on concentration for OH-Telagen-S, 242 AM-148 AH in benzene at 37°C. (\bar{M}_n) = 1950 \pm 50

Benzene appears to be an acceptable solvent for Telagen-S. The slope of $\Delta R/C$ plotted against the concentration is small and the extrapolation error is correspondingly reduced.

Comparison of \bar{M}_n in Different Solvents

In Figure 5, apparent \bar{M}_n data were obtained at various concentrations in benzene and in 1,2-dichloroethane for Telagen-S. Although different calibrating substances were used (benzil was the calibrant in the case of benzene solvent), closely comparable (\bar{M}_n)₀ values are obtained for the polymer in the two solvent-calibrant systems. This lends confidence to the absolute accuracy of the VPO method in application to OH-Telagen-S.

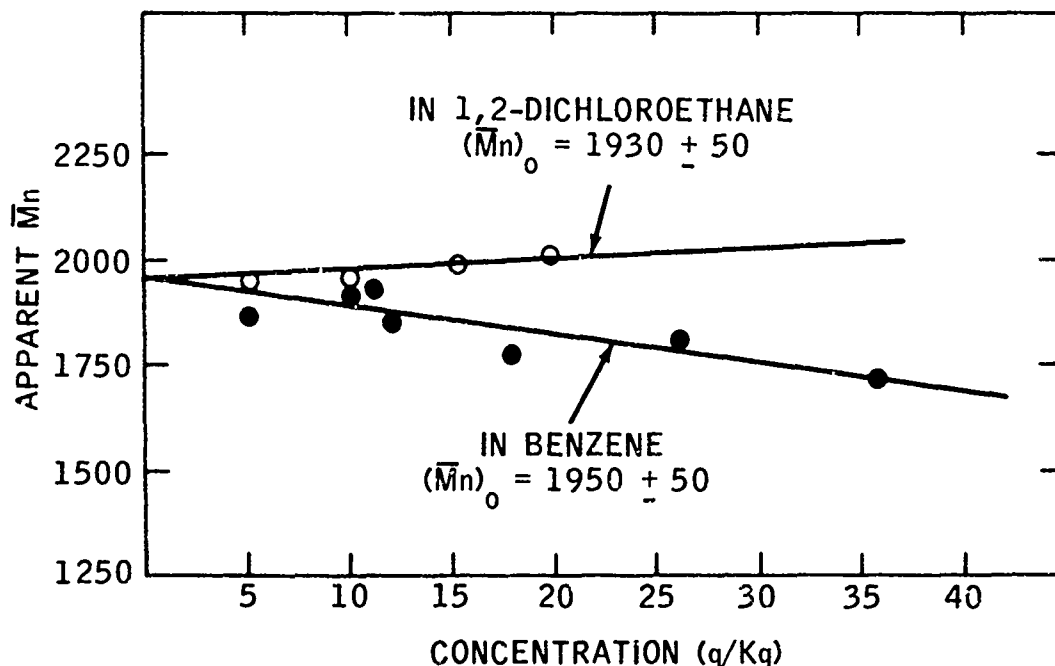


Figure 5. Dependence of apparent molecular weight (\bar{M}_n) on concentration for OH-Telagen-S, 242 AM-148 AH in two different solvents at 37°C

(b) Molecular Weight by Osmodialysis

The osmodialysis method is of value primarily for the information it provides as to molecular weight distribution, as discussed further in Section 1.5. The mean or average molecular weight calculated from osmodialysis data serves as a convenient way of describing the location of the approximate center of the distribution as a whole on the molecular weight scale. However, the osmodialysis method is correlative and not absolute as regards molecular weights. Primarily for this reason, the mean or average molecular weight data obtained by osmodialysis should not be used for the calculation of functionality of polymers.

The average molecular weight calculated from the histogram was 1450. This is significantly lower than the number average molecular weight determined by VPO (1950).

The molecular weight data on Telagen-S by osmodialysis indicate that the polar end group (OH) of the polymer does alter somewhat its permeability through the cellophane membrane and that the osmodialysis calibration based on hydrocarbon polymers without polar end groups is not strictly applicable to Telagen-S. A possible explanation which could account for the apparent lower molecular weight is that some chemical interaction takes place between the hydroxy end groups of the polymer and the cellophane membrane which effectively increases the permeation rate of the polymer through the membrane and hence gives a lower apparent molecular weight.

1.2. Equivalent Weight Determination

Equivalent weight measurements of OH-Telagen-S were made by three independent methods: (1) by measuring the intensity of the absorption band of the hydroxyl group in the infrared, (2) by the Diborane Method and (3) by reaction with toluenesulfonyl isocyanate (TSNCO). Results of the equivalent weight measurements by these three methods are discussed below.

(a) Equivalent Weight Determination by Infrared

An infrared calibration was established for determining the OH-equivalent weight of Telagen-S on the basis of sec-butanol reference blends in a 25 vol. % ethyl acetate/75 vol. % carbon tetrachloride solvent mixture (see Appendix B-1). The calibration was determined with the aid of a Beckman IR-8. The infrared method measures the intensity of the hydroxyl stretching mode absorption of hydroxy-terminated prepolymers in solution. The success of this analysis stems from the use of a hydrogen bonding diluent, such as ethyl acetate, which effectively eliminates the difference in molar extinction coefficients that are typically observed among alcohols of different molecular structure. Since ethyl acetate is not a solvent for Telagen-S, we used a solvent mixture of 25 vol. % ethyl acetate and 75 vol. % carbon tetrachloride.

OH absorbance was measured at 2.74 microns and 2.82 microns as a function of solution concentration. A 0.1055 mm thick liquid absorption cell was used to measure the intensity of the absorbance. A background correction was measured by drawing a base line between 2.65 μ and 3.95 μ .

The hydroxyl end group analysis by infrared and hence the apparent equivalent weight determination was found to be independent of the Telagen-S concentration in the solvent mixture below a concentration of 25 wt. % (35 vol. %). Above this concentration, the OH absorbance became nonlinear with polymer concentration and consequently the apparent equivalent weight increased rapidly. This is graphically depicted in Figure 6.

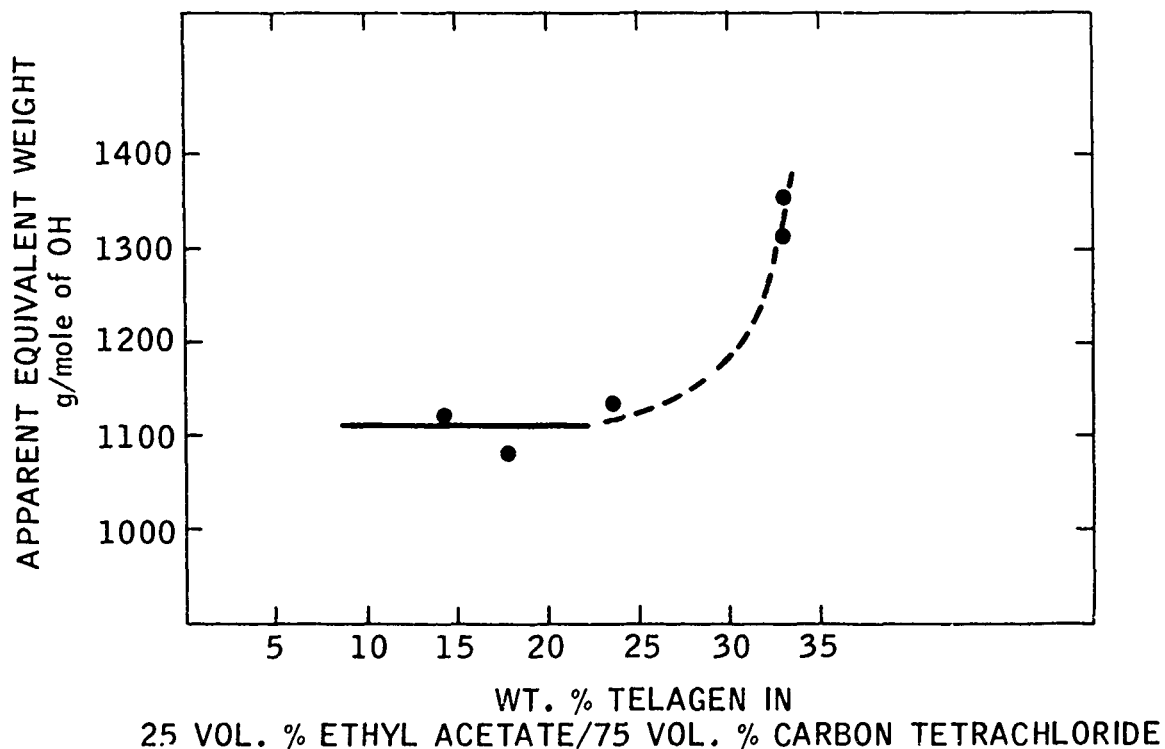


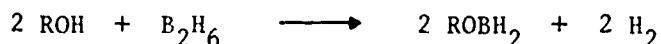
Figure 6. Equivalent weight determination of OH-Telagen-S, 252 AM-148 AH by IR in 25 vol. % ethyl acetate/75 vol. % carbon tetrachloride. Effect of concentration on apparent equivalent weight,

Apparently, above a 25 wt. % solution of Telagen-S, polymer-polymer bonding through the polar end group becomes significant. All subsequent equivalent weight determinations were therefore carried out at concentrations below 25 wt. %. Measurements obtained by the IR equivalent weight method at a given concentration were reproducible with 2%. The average value of three determinations by IR was 1110 grams of Telagen-S/mole of OH. Aerojet has reported an equivalent weight of 1100 g/mole of OH (0.91 meg/g) which is in excellent agreement with our IR values.

(b) Equivalent Weight Determination
by the Diborane Method

In order to obtain a comparison of the equivalent weight data by IR with an independent method, we have extended our equivalent weight measurements to the Diborane method. This method is an independent chemical method which was primarily set up as an independent method for the equivalent weight determination of P-BEP.

The Diborane method was developed by Aerojet. Basically the method involves the reaction of Diborane with protonic material and measuring, manometrically, the evolved hydrogen.



The analysis is quite rapid, requiring about a half hour per analysis. Its disadvantage is the fact that the material is consumed during the analysis whereas the infrared analysis allows recovery of the test sample.

Calibration of the test apparatus was carried out with n-butanol of better than 99.9% purity.

A series of Diborane analyses have yielded the following data:

Equivalent weight (grams/mole of OH)

	1070
	1040
	1030
	1060
	1050
	<u>1090</u>
Average	<u>1060</u> grams/mole of OH

The average value of these 6 determinations is 1060 grams of polymer/mole of OH, which is about 4.5% lower than the average equivalent value determined by IR. This difference is small but significant in view of the fact that this percentage change is directly reflected in the functionality, calculated from the ratio of molecular weight to equivalent weight.

(c) Equivalent Weight Determination of
Telagen-S by Reaction with
Toluenesulfonyl Isocyanate (TSNCO)

To determine the feasibility of the approach described in Section A, as an accurate hydroxyl-equivalent weight method of prepolymers, we tested the method on Telagen-S, 242 AM-198 AH, a material which had been characterized by a number of different equivalent weight methods. Solutions of Telagen-S and toluenesulfonyl isocyanate (in excess) of known concentrations in CHCl_3 were prepared in a dry box. Infrared spectra were subsequently obtained at room temperature at given time intervals. The time dependence of the NCO absorbance at 4.47μ for two Telagen-S/TSNCO solutions is shown in Figures 7 and 8.

Figure 7. Reaction of OH-Telagen-S, 242 AM-148 AM with toluenesulfonyl isocyanate in chloroform at room temperature. Change of isocyanate absorbance at 4.47 μ with time. Concentration as indicated.

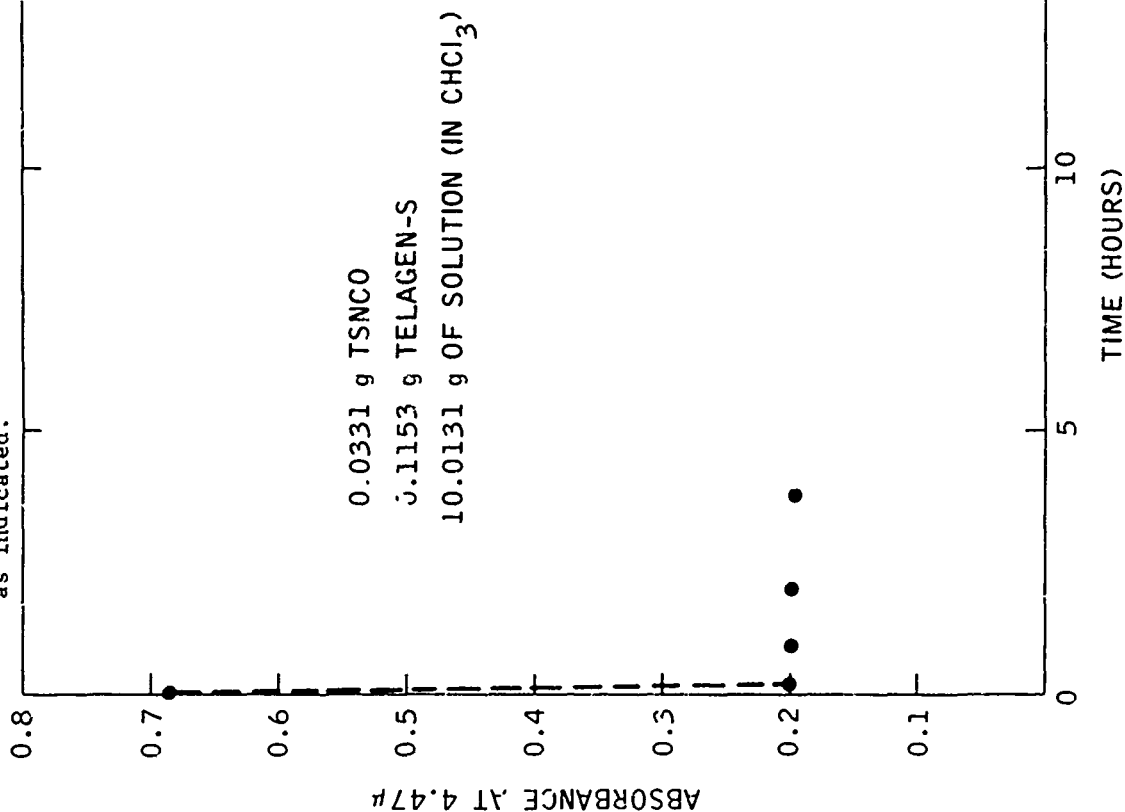
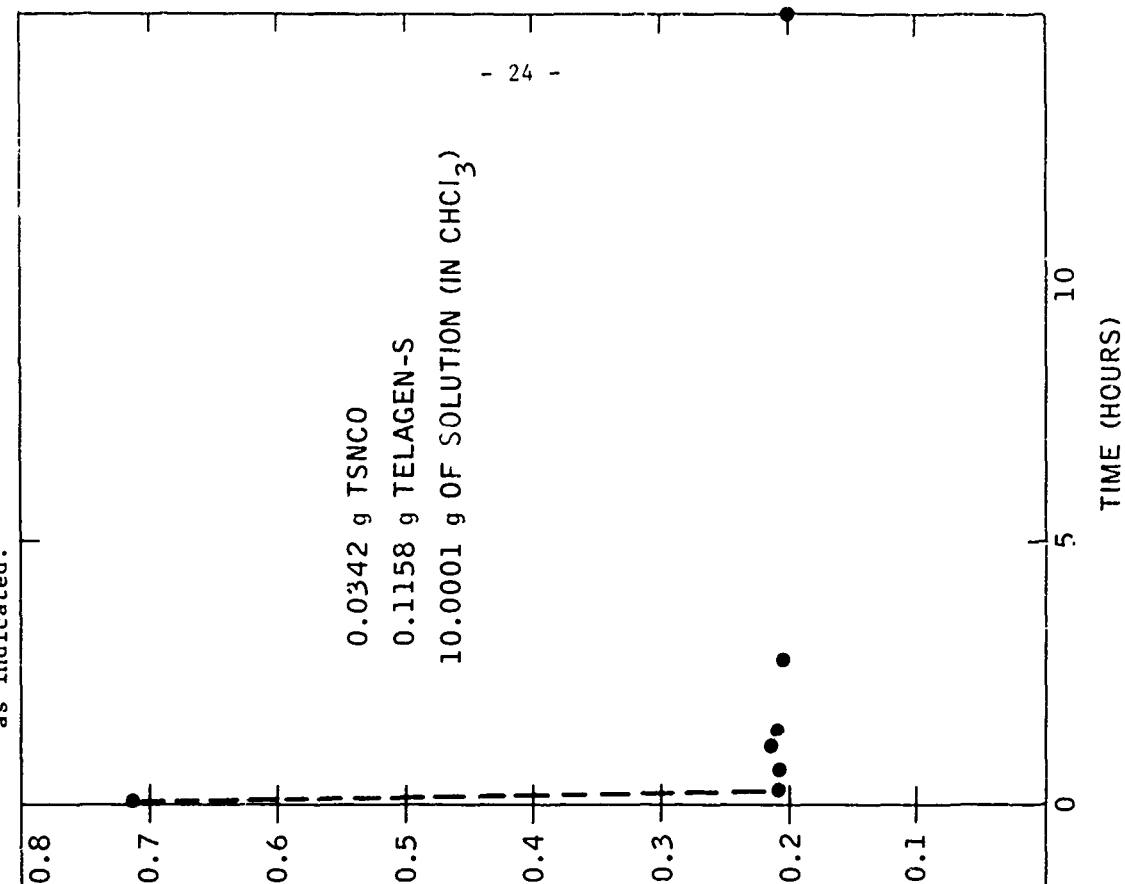


Figure 8. Reaction of OH-Telagen-S, 242 AM-148 AM with toluenesulfonyl isocyanate in chloroform at room temperature. Change of isocyanate absorbance at 4.47 μ with time. Concentration as indicated.



Pertinent observations can be summarized as follows:

- The reaction between Telagen-S and TSNCO (in excess) at room temperature is extremely rapid. The reaction is complete in less than 15 minutes (the time at which the first IR spectrum was taken). This high reaction rate is typical for primary and secondary alcohol groups with TSNCO as reported in the literature.
- Because of the extremely high reaction rate of this isocyanate with hydroxyl groups the initial isocyanate absorbance at zero time is obtained from the calibration plot.
- The absorbance at 4.47μ remains constant after 15 minutes indicating that the OH-NCO reaction is complete.

The calculated equivalent weight of Telagen-S based on these two measurements is:

$$\begin{array}{r} 1100 \\ 1080 \\ \hline \text{Average: } 1090 \text{ grams/mole of OH} \end{array}$$

This compares well with the equivalent weight determined by IR based on OH absorption intensity (1110 grams/OH) and by the Diborane method (1060 grams/OH).

These data show that the approach is sound and that the method is applicable to Telagen-S.

It should be emphasized that because of the high reactivity of this isocyanate it is essential that all solutions are prepared under dry box conditions. Moisture will readily react with this isocyanate.

The study of the isocyanate/prepolymer reaction was extended to an additional isocyanate, p-nitrophenyl isocyanate. Similar reaction studies with Telagen-S and p-nitrophenyl isocyanate showed that the reaction is much slower as compared to the corresponding reaction with toluenesulfonyl isocyanate. In fact, the reaction is still incomplete after 42 hours at room temperature (see Figure 9). P-nitrophenyl isocyanate is, therefore, not suited for a rapid equivalent weight determination of hydroxy-terminated prepolymers.

It appears, therefore, that sulfonyl isocyanates may be the only class of isocyanates suitable for the rapid determination of the equivalent weight of hydroxy-terminated prepolymers by this method.

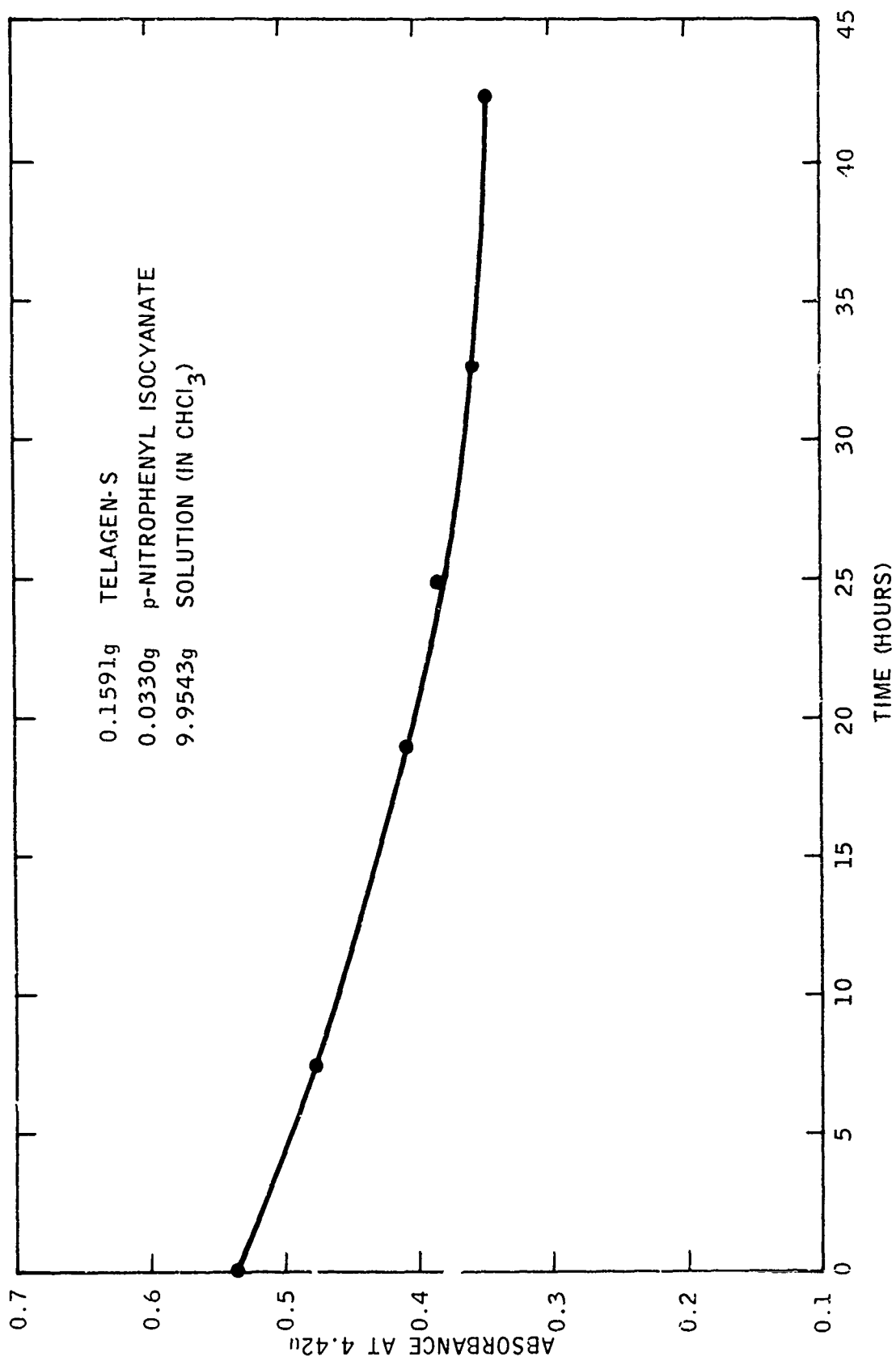


Figure 3. Reaction of OH-Telagen-S, 242 AM-148 AH with p-nitrophenyl isocyanate in dilute chloroform solution at room temperature. Change of isocyanate absorbance at 4.42μ with time. Concentration as indicated.

1.3. Functionality Determination

Functionality of a prepolymer is defined as the ratio of number-average molecular weight to equivalent weight and can therefore be calculated from separate measurements of molecular weight and equivalent weight.

From the extrapolated molecular weights $(\bar{M}_n)_0$ by VPO in benzene and in 1,2-dichloroethane [average $(\bar{M}_n)_0 = 1940$] and the equivalent weight determinations based on the three methods discussed in the preceding section the calculated functionalities are:

<u>Equivalent Weight Method</u>	<u>Equivalent Weight (grams/mole of OH)</u>	<u>Functionality</u>
Infrared	1110	1.75
Diborane	1060	1.83
Toluenesulfonyl Isocyanate	1090	1.78

The above functionalities are significantly below the theoretical functionality of 2.0 and therefore suggested the presence of mono-and/or nonfunctional components. Since no method was known which could determine the functionality distribution of hydroxy-functional prepolymers we carried out some exploratory studies to develop a method which could effectively fractionate prepolymers into non-, mono- and difunctional components.

1.4. Functionality Distribution Measurements

A separation technique which can separate prepolymers by functionality rather than molecular weight was first developed for the OH-Telagen-S prepolymer and subsequently extended to COOH-functional prepolymers. The method is based on the adsorption of prepolymer on activated silica gel and subsequent selective desorption by stepwise elution using solvent mixtures of progressively greater elution power. Details of this technique are described below.

Fractionation of Telagen-S by Column Elution from Silica Gel

Two samples of Telagen-S, 242 AM-148 AH, were fractionated by step-wise elution from 100-200 mesh silica gel. The polymer was placed on the column in an approximate 50 wt.% solution in CCl_4 . The polymer was eluted from the column by step-wise addition of CCl_4 , CHCl_3 , CH_2Cl_2 and solvent mixtures of $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ and finally CH_3OH . Polymer recovery was found to be dependent on the silica gel/polymer ratio. At a ratio of 20/1, the total recovery was 96.5% whereas at a gel/polymer ratio of 80/1, the recovery was only 87.9%. The elution response at this latter gel/polymer ratio is graphically summarized in Figure 10. Molecular weight measurements $((\bar{M}_n)_0$ by VPO) and equivalent weight data by IR were obtained on all fractions and are summarized below.

Fractionation of Telagen-S, 242 AM-148 AH
by Column Elution from Silica Gel

Identification: 369-63

Silica gel/polymer ratio: 80/1

Total polymer recovery. 87.9%

<u>Fraction</u>	<u>Wt.% of Total</u>	<u>(\bar{M}_n)_o</u>	<u>Equivalent Weight (grams/OH)</u>	<u>Functionality</u>
I	5.0	1760 \pm 30	∞ *	0
II	9.23	3200 \pm 150	3140	1.02
III	10.10	2030 \pm 50	2060	0.98
IV	3.26	**		
V	6.12	1580 \pm 50	1355	1.17
VI	12.39	2060 \pm 60	970	2.12
VII	12.90	1850 \pm 40	890	2.08
VIII	12.37	1620 \pm 60	790	2.05
IX	16.54	1700 \pm 60	800	2.12

* This fraction showed no OH absorption bands at either 2.75 μ or 2.82 μ .

** Fraction IV contained a solid non-polymeric component of M.P. 126-132°C which was isolated by vacuum sublimation. This solid component accounted for about 0.7 wt.% of the total polymer charged. This is believed to be the same material which had previously been recovered from the total polymer by vacuum stripping.

Identification: 369-56

Silica gel/polymer ratio: 20/1

Total polymer recovery: 96.5%

<u>Fraction</u>	<u>Wt. of Total</u>	<u>\bar{M}_n</u>	<u>Equivalent Weight</u> <u>(grams/OH)</u>	<u>Functionality</u>
I	8.63	2310 \pm 50	9900	0.23
II	22.0	1960 \pm 40	1900	1.03
III	12.75	2270 \pm 50	1420	1.60
IV	5.45	2250 \pm 60	1100	2.04
V	19.23	1830 \pm 50	880	2.08
VI	13.82	1870 \pm 30	945	1.98
VII	10.65	1680 \pm 40	875	1.93
VIII	4.00	1400 \pm 20	680	2.06

These fractionation studies of Telagen-S reveal some interesting facts:

- Telagen-S contains significant components of both mono- and non-functional components.
- About 5 wt.% of the polymer has zero functionality. The molecular weight of this fraction is about the same as that of the total polymer indicating that the non-functional polymer is not concentrated in either the low or high molecular weight range.
- 20 to 30% of the polymer is monofunctional, the remainder being difunctional.
- This separation technique essentially fractionates the polymer by functionality rather than molecular weight.
- More efficient separation is obtained at the higher gel/polymer ratio (80/1). However, the higher separation efficiency is offset by a greater loss on the column (% recovery = 87.9%).

This fractionation study proves rather conclusively the presence of non-, mono- and difunctional components in Telagen-S. In view of these data, it should be possible to improve the mechanical properties of the Telagen-S binder if synthesis conditions can be established which effectively eliminate or reduce the formation of mono- and non-functional components.

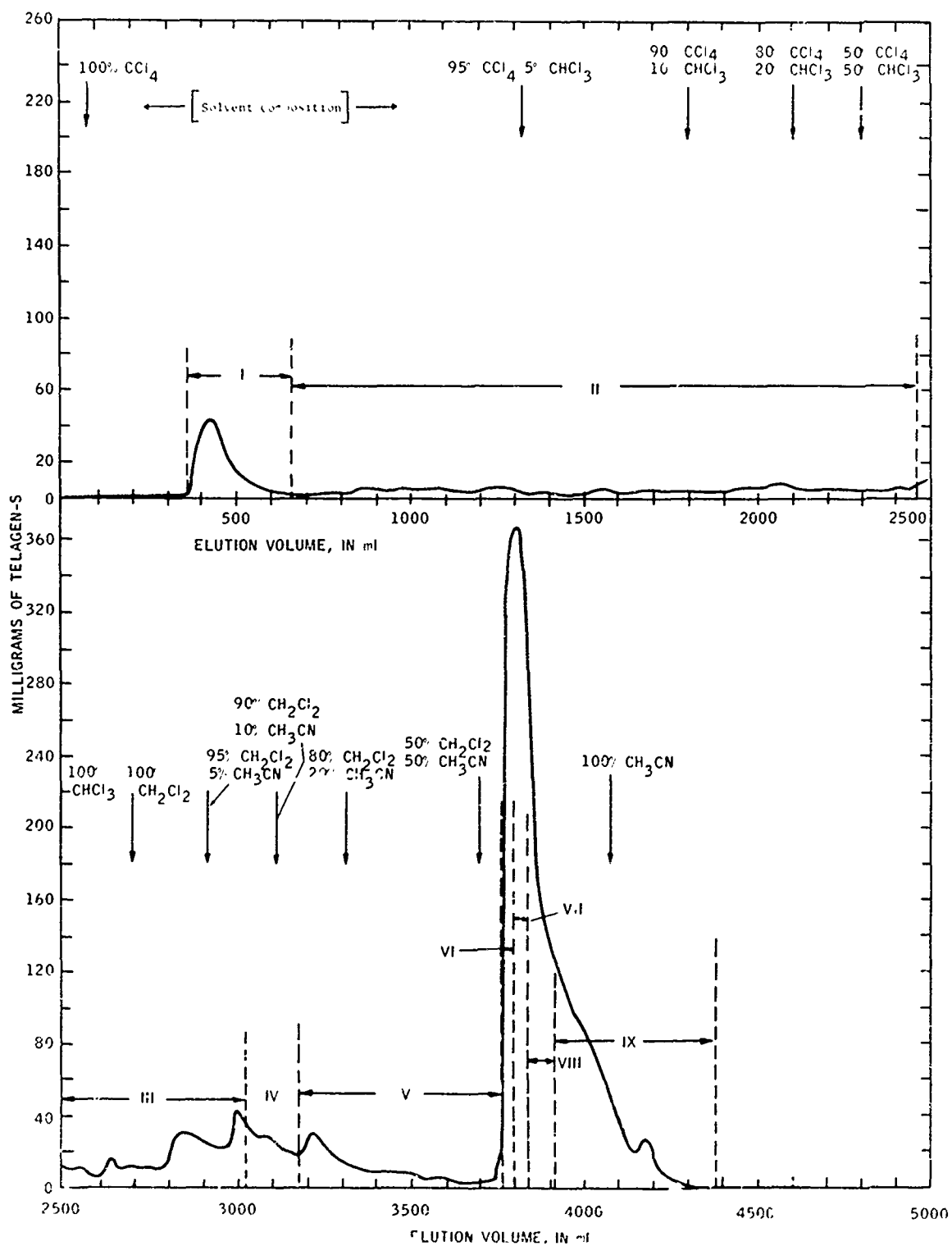


Figure 10. Fractionation of OH-Telagen-S. 242 AM-148 AH by elution from silica gel - elution profile run 369-63.

We subsequently carried out additional fractionation studies to check the reproducibility of this fractionation technique and to obtain a better definition of the amount of monofunctional polymer present. The technique was similar to that reported previously: a slurry of silica gel in 100% CCl_4 was charged to the column. The polymer was placed on the column in an approximate 70 wt % solution in CCl_4 . The polymer was eluted from the column by stepwise addition of CCl_4 , solvent mixtures of $\text{CCl}_4/\text{CHCl}_3$, CHCl_3 , solvent mixtures of $\text{CH}_2\text{Cl}_2/\text{CHCl}_3$, CH_2Cl_2 , and finally $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ solvent mixtures. Fractionations were carried out at two different silica gel/polymer ratios (155/1 and 87/1) and slightly different solvent compositions of the eluting solvents. In one case, the column was provided with a cooling jacket and the fractionation was carried out at a temperature of 10-15°C. Under these conditions the difunctional Telagen-S components showed considerable tailing, presumably because of the reduced solubility of the polymer at the lower temperature. The fractionation was prematurely terminated at a recovery of 84.9 wt %.

The eluting solvent was collected in 40 ml fractions and in a typical fractionation about 130 fractions are collected. All fractions were subsequently stripped to constant weight under vacuum at 40-50°C. Based on the weight of polymer collected an elution profile was constructed. The small individual fractions were then combined into three to five major fractions. These major fractions were stripped again to constant weight and characterized.

The elution profiles of two fractionation studies are shown in Figures 11 and 12. Molecular weight measurements ($(\text{Mn})_0$ by VPO) and equivalent weight data are summarized below.

Fractionation of Telagen-S, 242 AM-184 AH
by Gradient Solvent Elution from Silica Gel

Identification: 369-71

Silica gel/polymer ratio: 155/1

Polymer charged to column: 2.574 grams

Total polymer recovery: 94.8%

Temperature: 24°C

<u>Fraction</u>	<u>Wt % of Total</u>	<u>(\bar{M}_n)₀</u>	<u>Equivalent Weight (grams/OH)</u>	<u>Functionality</u>
I	5.3	1760	∞^*	0
II	25.0	2270	2100	1.08
III	5.0	1590	1210**	1.31
IV	52.0	1910	920	2.08
V	<u>7.5</u> 94.8%	1860	910	2.04

* This fraction showed no OH absorption bands at either 2.75 μ or 2.82 μ .

** Equivalent weight in doubt because of sample size limitation.

Identification: 369-73

Silica gel/polymer ratio: 87/1

Polymer charged to column: 4.6109 g

Total polymer recovery: 84.9%**

Temperature: 10-15°C

<u>Fraction</u>	<u>Wt % of Total</u>	<u>(\bar{M}_n)₀</u>	<u>Equivalent Weight (grams/OH)</u>	<u>Functionality</u>
I	5.2		∞^*	0
II	25.2	2270	2240	1.01
III	<u>54.5</u> 84.9%**	1730	850	2.04

* This fraction showed no OH absorption bands at either 2.75 μ or 2.82 μ .

** Fractionation was prematurely terminated.

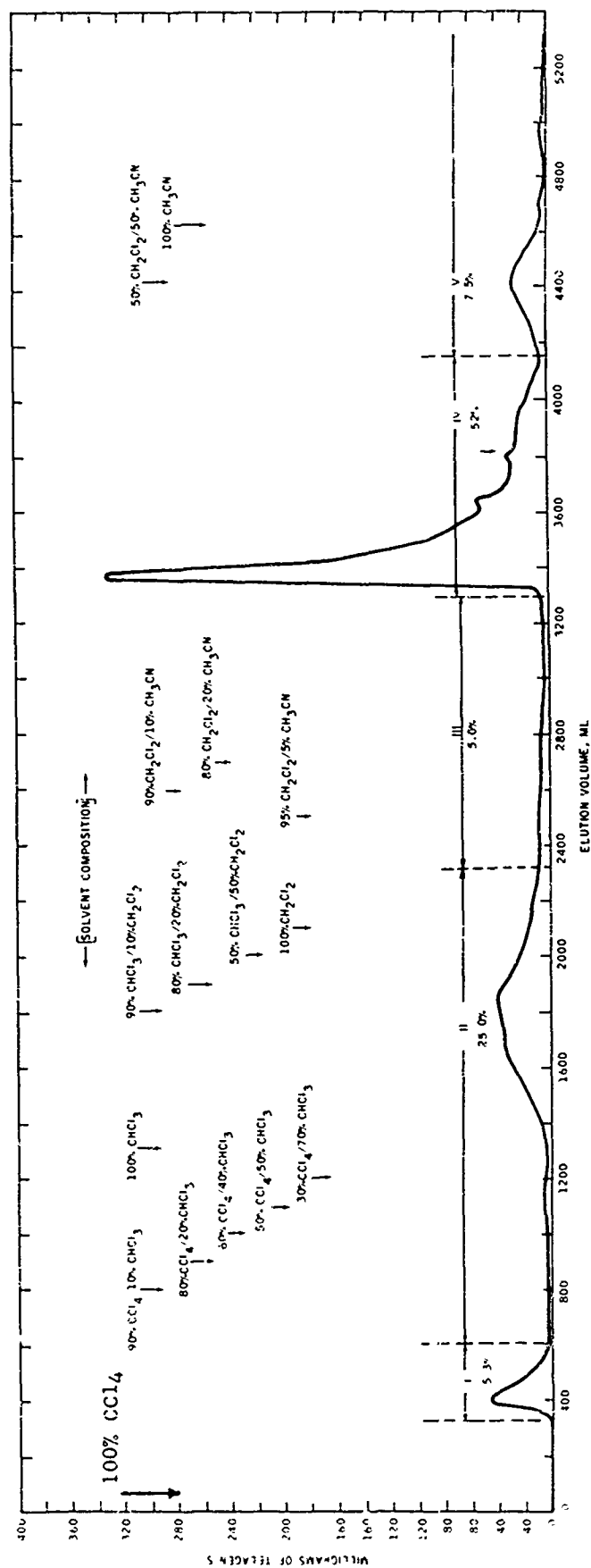


Figure 11. Fractionation of OH-Telagen-S, 242 AM-148 AH by gradient solvent elution from silica gel; elution profile of run 369-71. Silica gel/polymer ratio = 155/1.

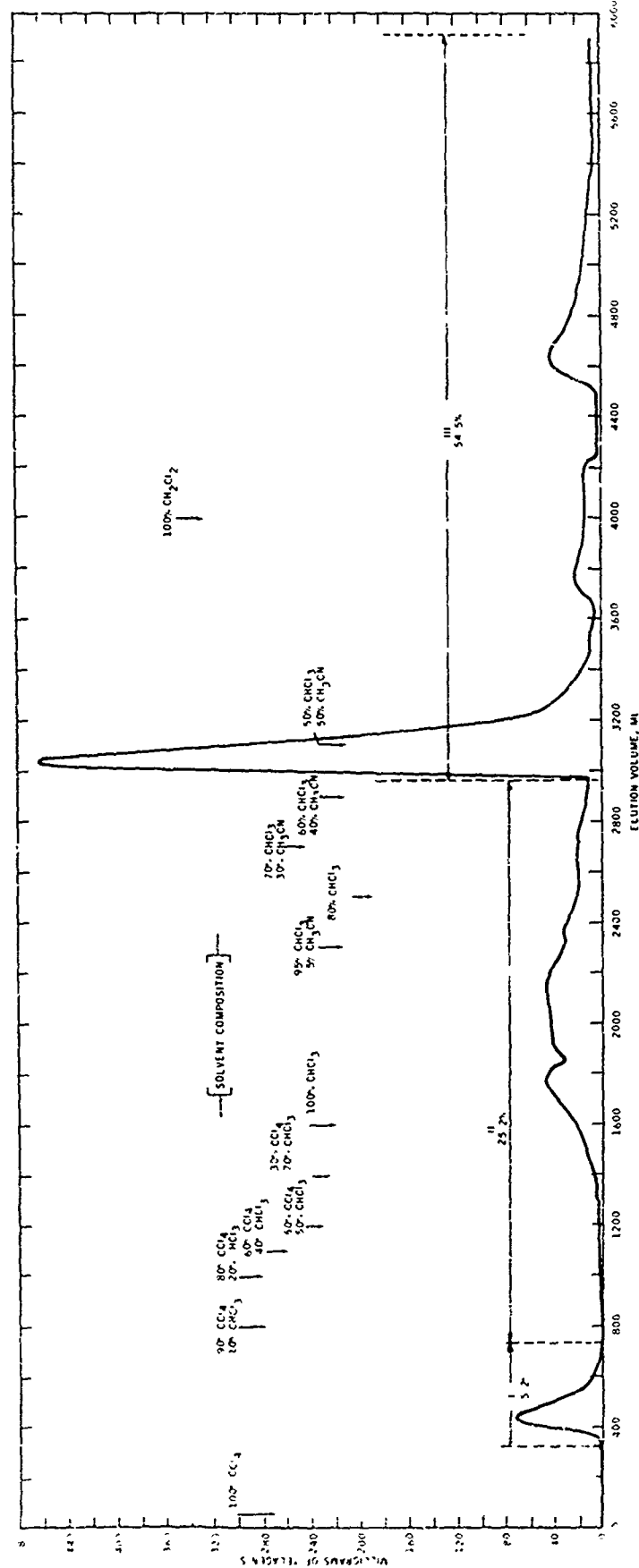


Figure 12. Fractionation of OH-Telagen-S, 242 AM-148 AH by gradient solvent elution from silica gel; elution profile of run 369-73. Silica gel/polymer ratio = 87/1.

These fractionation results support the previous tentative conclusions with respect to the functionality distribution of OH-Telagen-S.

- These latest results confirm that Telagen-S, 242 AM-184 A1, contains significant components of both non- and mono-functional components.
- 5.2 to 5.3 wt % of the polymer is nonfunctional. These figures agree well with the data previously reported for fractionation run 369-63 (5.0 wt % nonfunctional Telagen-S).
- The amount of monofunctional polymer can now be more clearly defined; it accounts for more than 25 wt % but less than 30 wt % of the total polymer.

Infrared Spectra of Non-, Mono- and Difunctional Telagen-S Fractions

The infrared spectra of three Telagen-S fractions representing non-, mono and difunctional components are shown in Appendix B-1. For comparison, we have also included the spectrum of the whole Telagen-S polymer. These spectra were taken on capillary polymer layers between NaCl plates. In general, these spectra reveal no essential differences except for the relative intensity of the hydroxyl band absorption. The whole polymer shows OH absorption at 3.0μ . In addition, the polymer exhibits absorption bands at 9.0 and 9.5μ . These bands are normally associated with the C-O stretching vibration of secondary (9.0μ) and primary (9.5μ) alcohols.

Figure 68 shows the spectrum of nonfunctional Telagen-S (369-71-I). This polymer fraction shows no absorption peaks at 3.0, 9.0 and 9.5μ .

Figure 69 represents the spectrum of monofunctional Telagen-S (369-71-II). The spectrum shows moderate absorption at 3.0, 9.0 and 9.5μ .

Figure 70 shows the spectrum of difunctional Telagen-S (369-71-IV) with correspondingly higher OH absorption peaks at 3.0, 9.0 and 9.5μ . It should be pointed out, however, that the OH absorption intensity of these neat polymer layers cannot be directly related to functionality since thickness of the layer and molecular weight must be considered.

We have also looked for possible evidence of crystallinity. Absorption at 13.7μ is generally considered evidence of crystallinity as in the case of polyethylene. Neither the whole Telagen-S polymer nor any of the above fractions show absorption peaks at 13.7μ . These spectra were taken at room temperature and therefore do not rule out the possibility of crystallinity at some lower temperature.

Molecular Weight Distribution of
Nonfunctional Components in
Telagen-S, 242 AM-184 AH by GPC

We obtained the molecular weight distribution of the non-functional components in Telagen-S (369-63-I) by gel permeation chromatography (see Figure 13).

The molecular weight distribution is based on a calibration using n-paraffin hydrocarbons. The molecular weight scale has not been adjusted to coincide with the number-average molecular weight determined by VPO $(Mn)_0 = 1760$.

The molecular weight distribution of this nonfunctional Telagen-S fraction is similar to that of the whole polymer. However, components in the low molecular weight region (200-700) are markedly enhanced in concentrations over the level observed in the whole polymer.

Ultraviolet Absorption Spectra of
Chromatographic Fractions of Telagen-S

A small quantity of a sublimable substance (fraction 369-63-IV) had been isolated by chromatographic fractionation of Telagen-S, 242 AM-148 AH. To gain further insight into its composition, the ultraviolet absorption spectrum of the sublimate was determined. For comparison, cuts II and III, which preceded cut IV in fractionation 369-63 were also examined (en toto, not sublimed). All three of these had been found to be monofunctional. In addition, a non-functional cut I from fractionation 369-67 was also examined.

The ultraviolet absorption spectrum of the sublimate (369-63-IV-S) revealed a strong absorption maximum at about 283 millimicrons. The spectral position and shape was typical of sterically hindered substituted phenols, and, further, was superimposable with the U.V. spectrum of 2,4-ditertiarybutyl phenol. (This does not necessarily identify the sublimate as being 2,4-ditertiarybutyl phenol but it suggests a related structure.) Such hindered phenols are frequently used as oxidation stabilizers. A similar but weaker U.V. absorption maximum was observed in the preceding cut III. Cut II and a non-functional cut I, however, exhibited only general absorption, increasing toward shorter wavelengths.

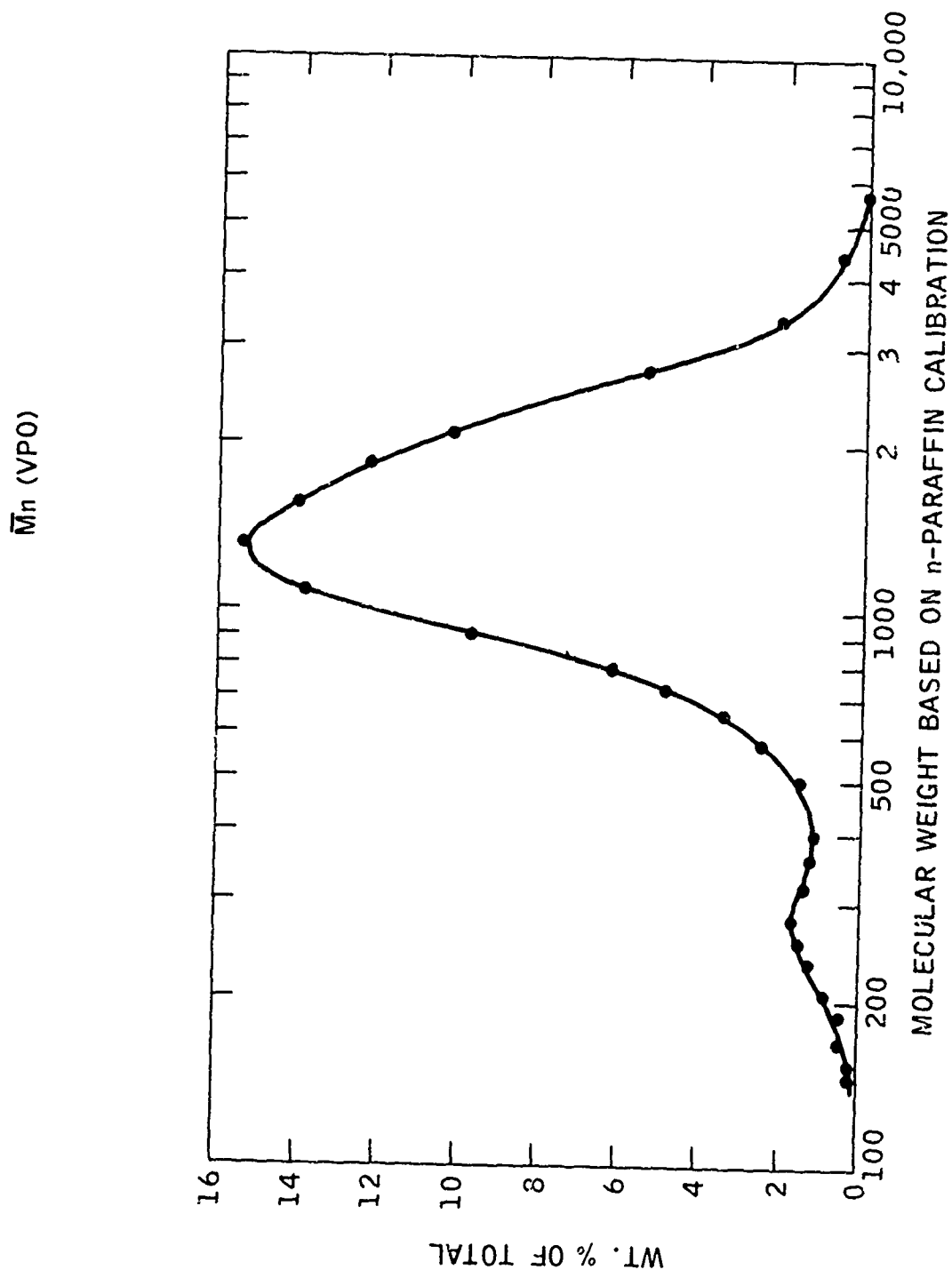


Figure 13. Molecular weight distribution of nonfunctional components in OH-Telagen-S, 242 AM-148 AH, fraction 369-63-I, by Gel Permeation Chromatography. Fraction 369-63-I corresponds to 5.0 wt.% of the total polymer. $(\bar{M}_n)_0$ by VPO is 1760.

U.V. Absorption Coefficients, 282 Millimicrons

<u>Specimen</u>	<u>Functionality</u>	<u>K, $\text{lg}^{-1} \text{ cm}^{-1}$</u>
369-67-I	0	0.0057 ^(a)
369-63-II	1	0.0385 ^(a)
369-63-III	1	0.0103 ^(b)
369-63-IVS	1	3.20 ^(b)

(a) General absorption increasing at shorter wave-lengths. No maximum in 220-400 mμ range.

(b) Absorption maximum, 283 mμ.

Re-Chromatography of Difunctional
OH-Terminated Telagen-S

To guard against the possibility that non- and/or monofunctional polymer is produced on the column as a result of dehydration by the adsorbent, we carried out one additional fractionation experiment, using difunctional OH-terminated Telagen-S previously isolated by solvent elution from silica gel.

The fractionation of difunctional Telagen-S was carried out under the same conditions previously used to separate the whole Telagen-S polymer into non-, mono- and difunctional components. The elution profile of difunctional Telagen-S is shown in Figure 14. The individual fractions were recombined into two major fractions: the front ends accounting for 22.6 wt.% of the polymer charged were combined into fraction I, the remainder was combined into fraction II. The apparent peak at about 1400 ml of elution volume is an artificial effect. The column had been shut down overnight at this point and was restarted the next morning. As a result, the polymer concentration in subsequent fractions was increased.

Molecular weight measurements (\bar{M}_n)₀ by VPO) and equivalent weight data are summarized below.

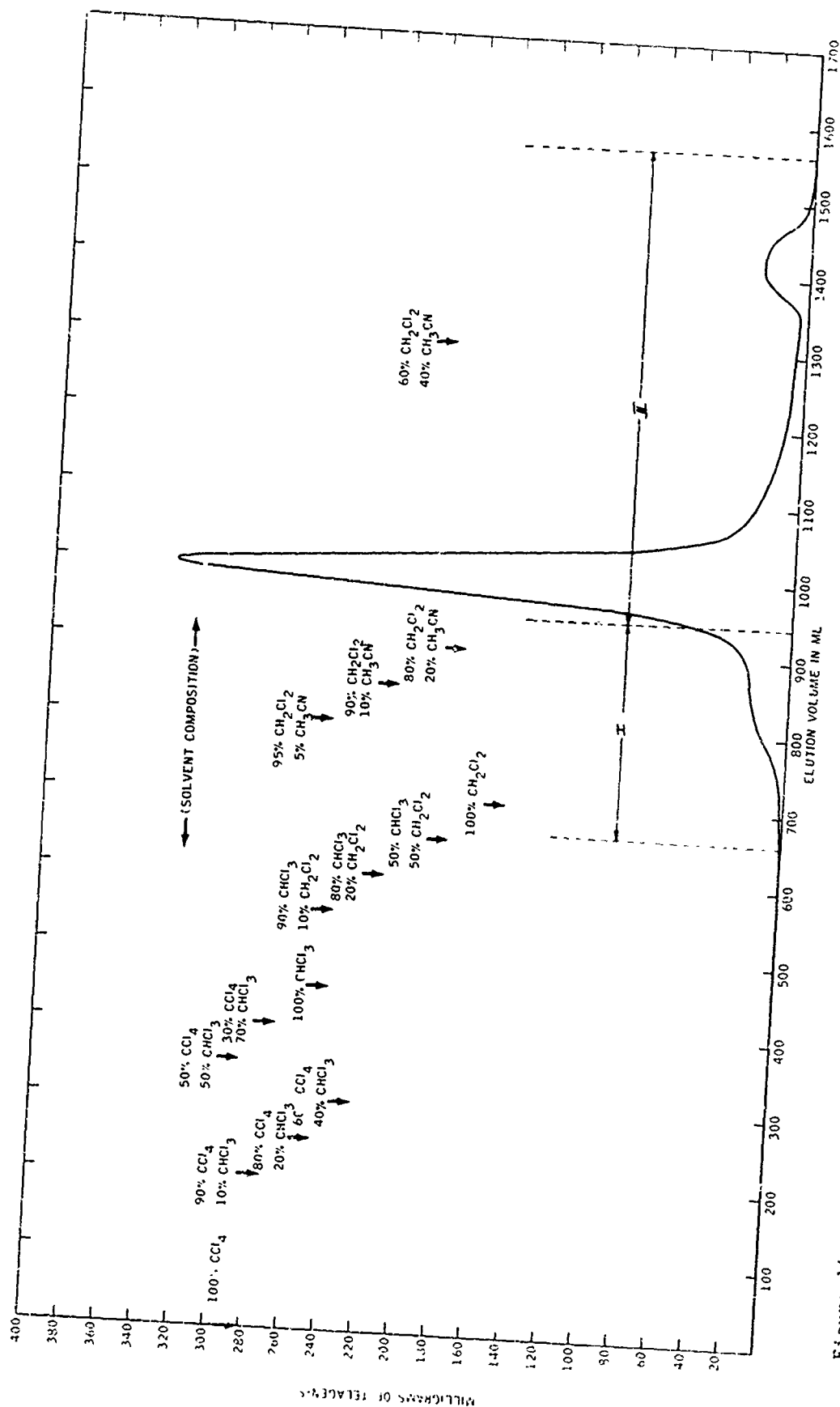


Figure 14. Re-fractionation of difunctional OH-Telagen-S by stepwise elution from silica gel; elution profile of run 369-77.

Re-fractionation of Difunctional Telagen-S, 369-75-II
by Stepwise Elution from Silica Gel

Identification: 369-77
Silica gel/polymer ratio: 110/1
Polymer charged to column: 0.809 g (369-75-II)
Total polymer recovery: 92.6%
Temperature: 24°C

Fraction	Wt.% of Total	\bar{M}_n	Equivalent Weight (grams/mole OH)	Functionality
Polymer charged to column	100.0	1650	830	1.99
I	22.6	1700	880	2.02
II	70.0	1530	760	2.01

These data show conclusively that none of the difunctional Telagen-S is converted to mono- or nonfunctional components on the column. Both the front end and the bulk of the eluted polymer is difunctional material.

1.5. Molecular Weight Distribution

The overall functionality of a bi-functional prepolymer has been defined as the ratio of the number-average molecular weight to the equivalent weight. To provide a more detailed picture of the nature of such a polymer, knowledge of the distribution of molecular weight and, ultimately, equivalent weight are necessary. Toward this objective, an intercomparison of two molecular weight distribution techniques was made. To aid this study, Telagen-S was separated into two fractions by adding methanol to a 10% solution of the polymer in chloroform. A precipitated high molecular weight portion amounting to 87% of the total polymer was obtained, and a 13% low molecular weight portion (not precipitated) was isolated from the remaining solution. These, as well as the whole polymer were subsequently examined by osmodialysis and by gel permeation chromatography.

(a) Osmodialysis

The osmodialysis method is based on the use of a recording membrane osmometer to follow the progress of a dialysis experiment. Interpretation of the record of the decay of apparent osmotic pressure with time, calibrations of the membrane and instrument used and other details are given in Appendix A-5.

A series of three osmodialysis runs were carried out in close succession on whole Telagen-S (solvent stripped). Data are summarized below in terms of the range of molecular sizes found, and the mean molecular weight.

Osmodialysis of CH-Telagen-S, 242 AM-148 AH,
Concentration 2 g/liter, toluene solvent, 35°C

<u>Range Found</u>		<u>Mean Mol. Wt.</u>
<u>Molecular Weight</u>	<u>DP</u>	
560-7800	10-140	1512
430-6800	8-120	1346
560-6400	10-115	<u>1480</u>
		1446

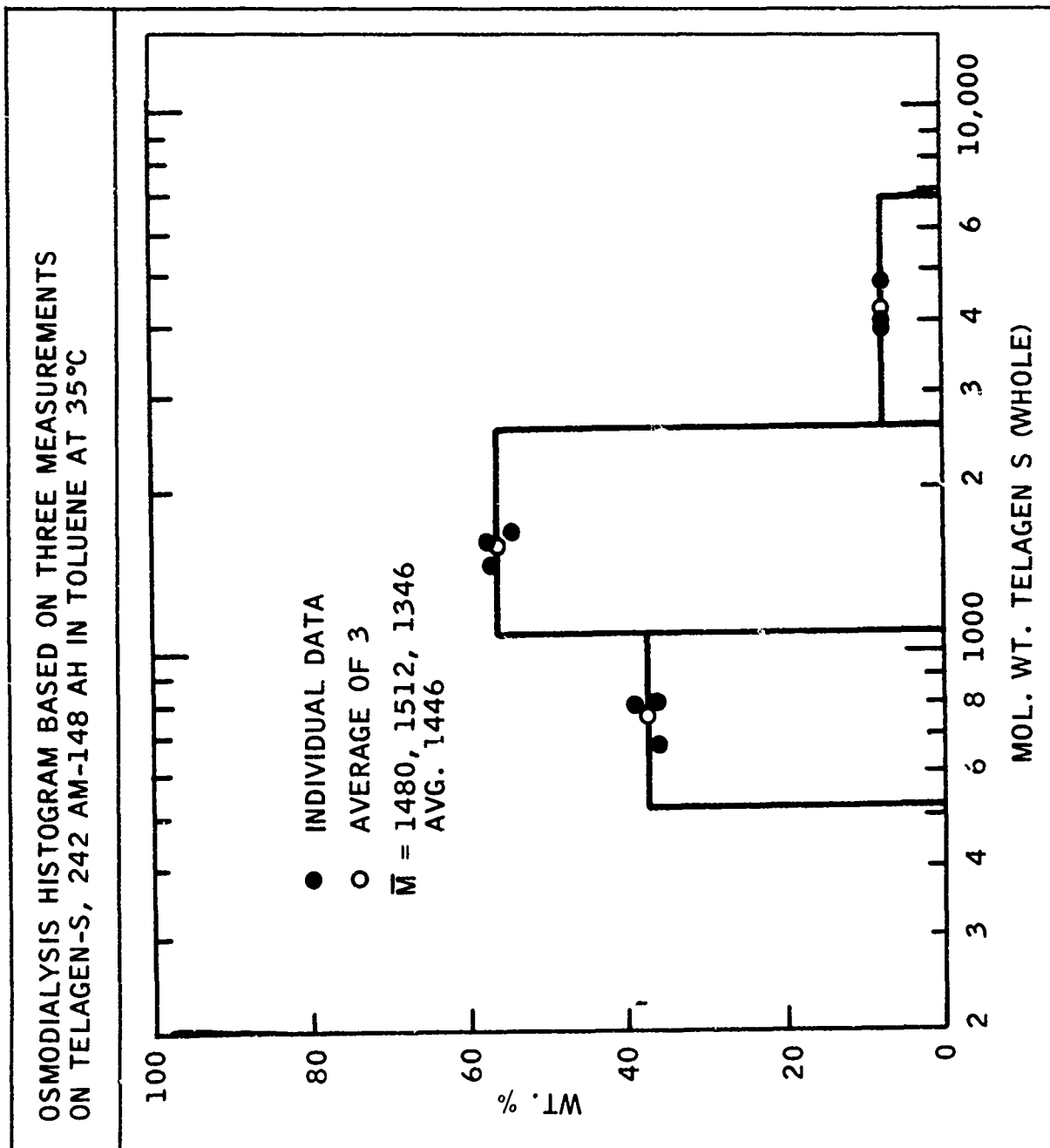
Nominally a narrow distribution polymer, Telagen-S is shown to contain a detectable concentration of molecular weight species ranging more than 10/1 in relative size. This observation is generally supported by GPC studies.

The most significant information obtained by osmodialysis is the molecular weight distribution which is depicted by the histogram in Figure 15. (Some of this information is also summarized in the table above.) The histogram of Telagen-S indicates a fairly wide molecular weight distribution ranging from a molecular weight of about 400 to 7000 which corresponds to a range of dp from about 10 to 125 monomer units. An asymmetry is noted in the distribution histogram, favoring the lower molecular weight species over the higher. Components in the 500-1000 molecular weight range are indicated to be several times more abundant than in the 2500-7000 range. The center of the distribution lies near 1500 (avg. \bar{M} calculated 1446).

For comparison with the whole polymer, the 87% high molecular weight portion previously separated by solvent participation was also examined. The osmodialysis histogram indicates that a substantial amount of low-molecular weight material has been removed. This is signified by a contraction from three resolvable blocks in the histogram for the whole polymer, Figure 15, to only two resolvable blocks in the histogram for the 87% heavy fraction, Figure 16. Species below 900 mol. wt. are indicated to be absent to the degree that they are no longer recognized as a separate sub-distribution. The principal block of the histogram remains centered at about 1500, and the higher molecular weights are still present. The mean molecular weight increased from \bar{M} avg. = 1446 for the whole polymer to 1740 for the 87% high molecular weight portion.

Substantial removal of low molecular weight species from the original polymer by solution precipitation is graphically confirmed by the osmodialysis histogram of the 13% low molecular weight fraction, Figure 17. The dominant molecular weights lie near the number-average molecular weight determined by PO ($M_n = 995$). It is also noted in Figure 17 that a five-fold concentration change does not dramatically affect the osmodialysis histogram for the 13% low molecular weight Telagen-S fraction.

Figure 15



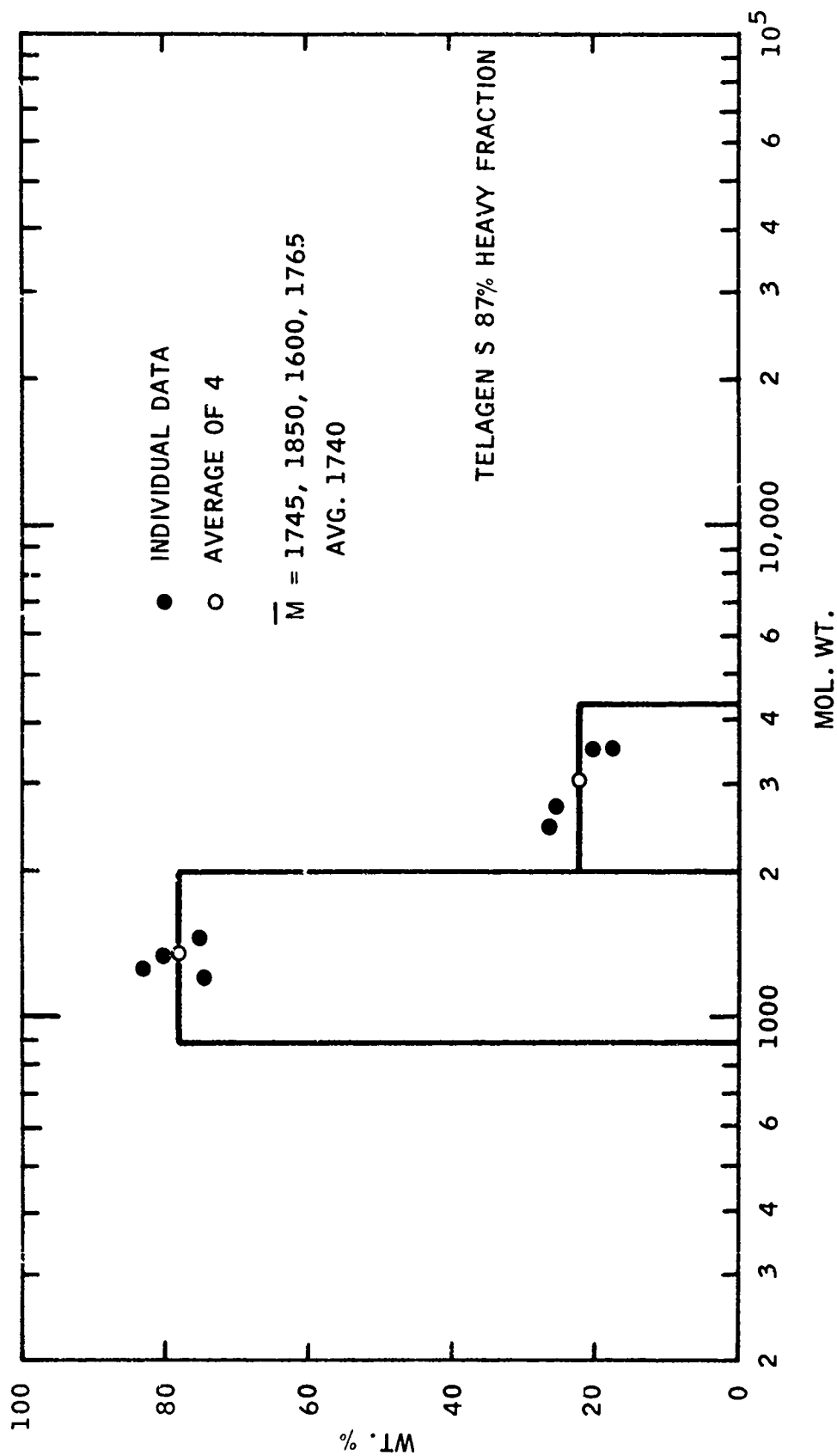


Figure 16 Osmodialysis histogram of the 87 wt.%, high molecular weight fraction of Telagen-S, in toluene at 35°C

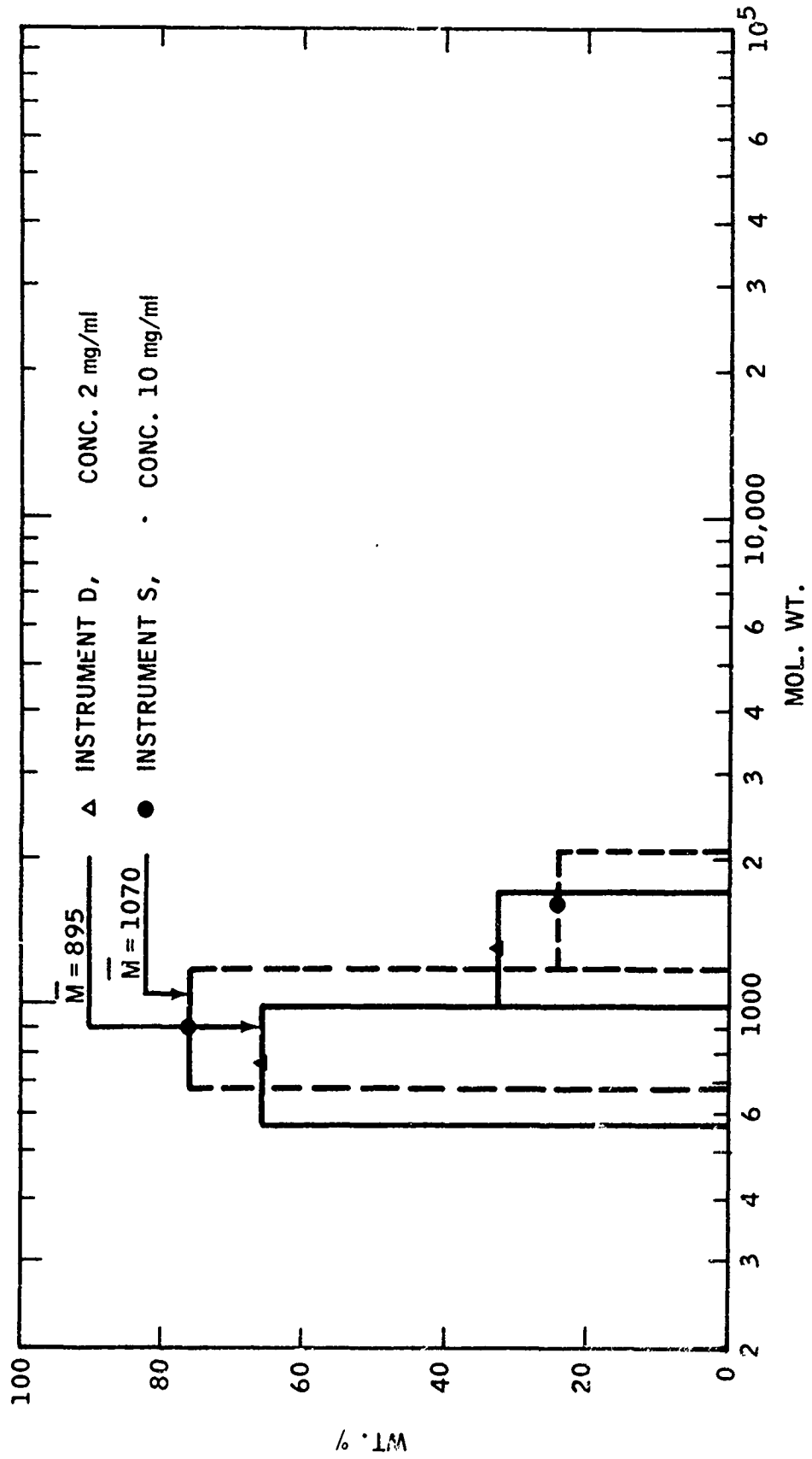


Figure 17. Osmodialysis histogram of the 13 wt.% low molecular weight fraction of Teligen-S in toluene at 35°C

(b) Gel Permeation Chromatography

Although the GPC technique is a comparatively recent development, it is now used in a large number of polymer research laboratories. The equipment employed, in the present case, and most often in other laboratories is the Analytical Gel Permeation Chromatograph developed and marketed by Waters Associates, Inc., Framingham, Mass. A general description of the GPC technique is given in Appendix A-5. The scheme employed for calibrating the instrument for analysis of Telagen-S and information as to types of columns used are also given.

The molecular weight distribution of Telagen-S as obtained by GPC is shown in Figure 18. The adjusted molecular weight scale has been made to coincide with the number-average value of 1950. The distribution can be seen to be sharply peaked at molecular weight 2300, but, in the nature of a Poisson distribution, tails extend downward to 400 and upward to 5000. In general, this is consistent with the range of molecular weights previously estimated to be present by osmodialysis (limit marks indicated in Figure 18).

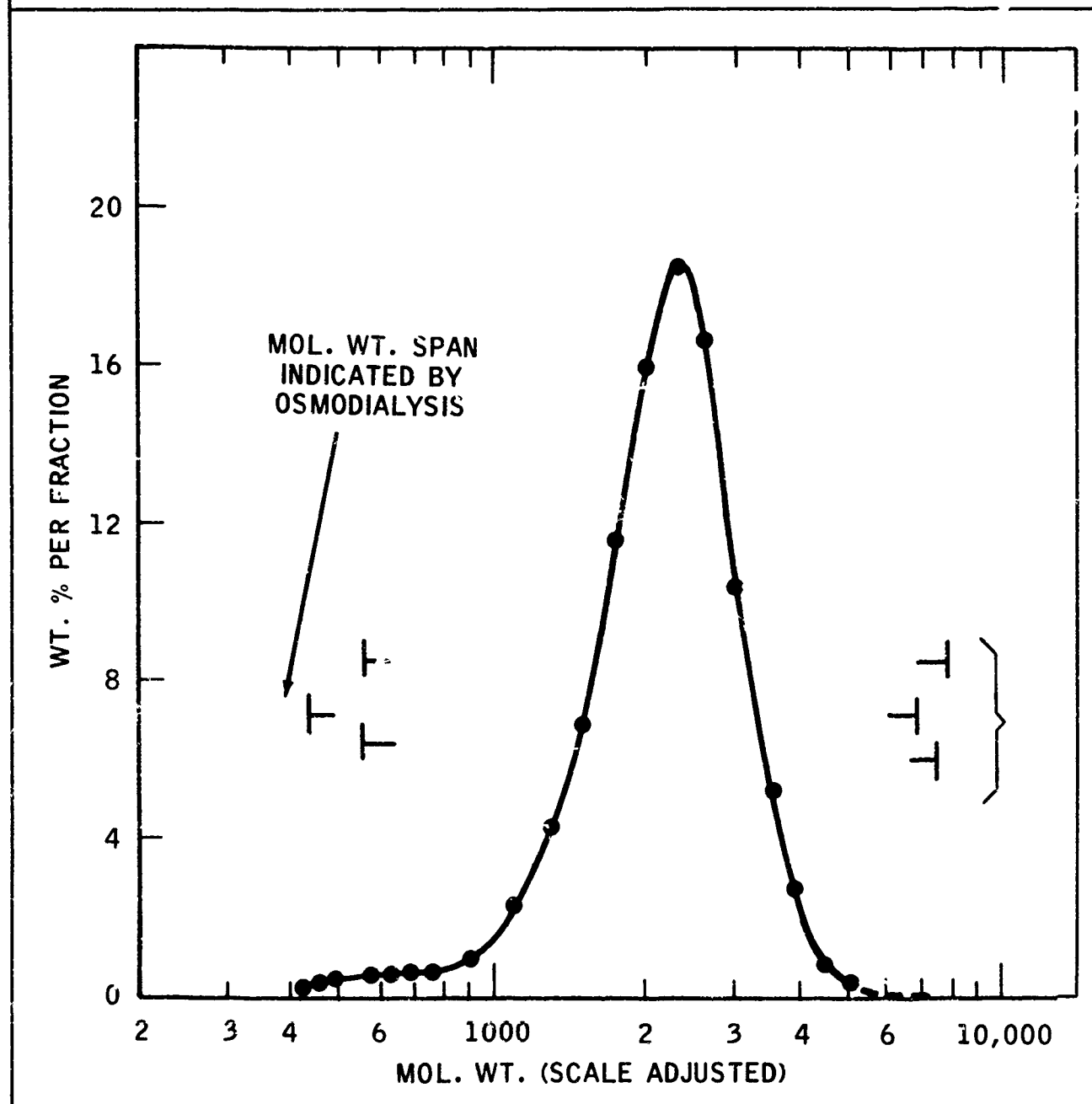
Both GPC and osmodialysis distribution methods indicate (but to different degrees) an asymmetry caused by a superabundance of low molecular weight species over high molecular species. This appears to be of marginal magnitude in the case of the GPC method (Figure 18) but is more pronounced in the osmodialysis histogram (Figure 15). Either distribution method is considerably more informative than M_n (1950) and $M_w/M_n = 1.2 \pm 0.1$. This ratio is obtained from gel permeation chromatography without scale adjustment.

Molecular weight distributions of the high and low Telagen-S fractions by gel permeation chromatography are shown in Figure 19. Since the high molecular weight fraction represents 87% of the original polymer, little change is noted relative to the unfractionated polymer except in the low molecular weight region. The distribution peak lies at 2300 m. wt. The curve representing the smaller (13%), low molecular weight portion has shifted to a lower position on the molecular weight scale, with the distribution peak at 1700. Components in the region of 300-1000 are markedly enhanced in concentration over the level observed in the whole polymer.

In general, the osmodialysis and gel permeation chromatography methods are in agreement as to the overall breadth of distribution of molecular weights in Telagen-S and the presence of a sharply peaked primary distribution. The two molecular weight distribution methods do differ, however, with regard to apparent selectivity with which low molecular weights were removed from the whole polymer by the solvent precipitation separation and, more specifically, with regard to the apparent distribution of molecular weights within the 13% low molecular weight Telagen-S fraction. This latter point is brought out graphically in Figure 20 in which the distributions as presented by the two methods are compared. The dashed and solid curves represent two slightly different methods of fitting a molecular weight scale to the GPC curves.

Figure 18

MOLECULAR WEIGHT DISTRIBUTION OF TELAGEN-S,
242 AM-148 AH BY GEL PERMEATION CHROMATOGRAPHY



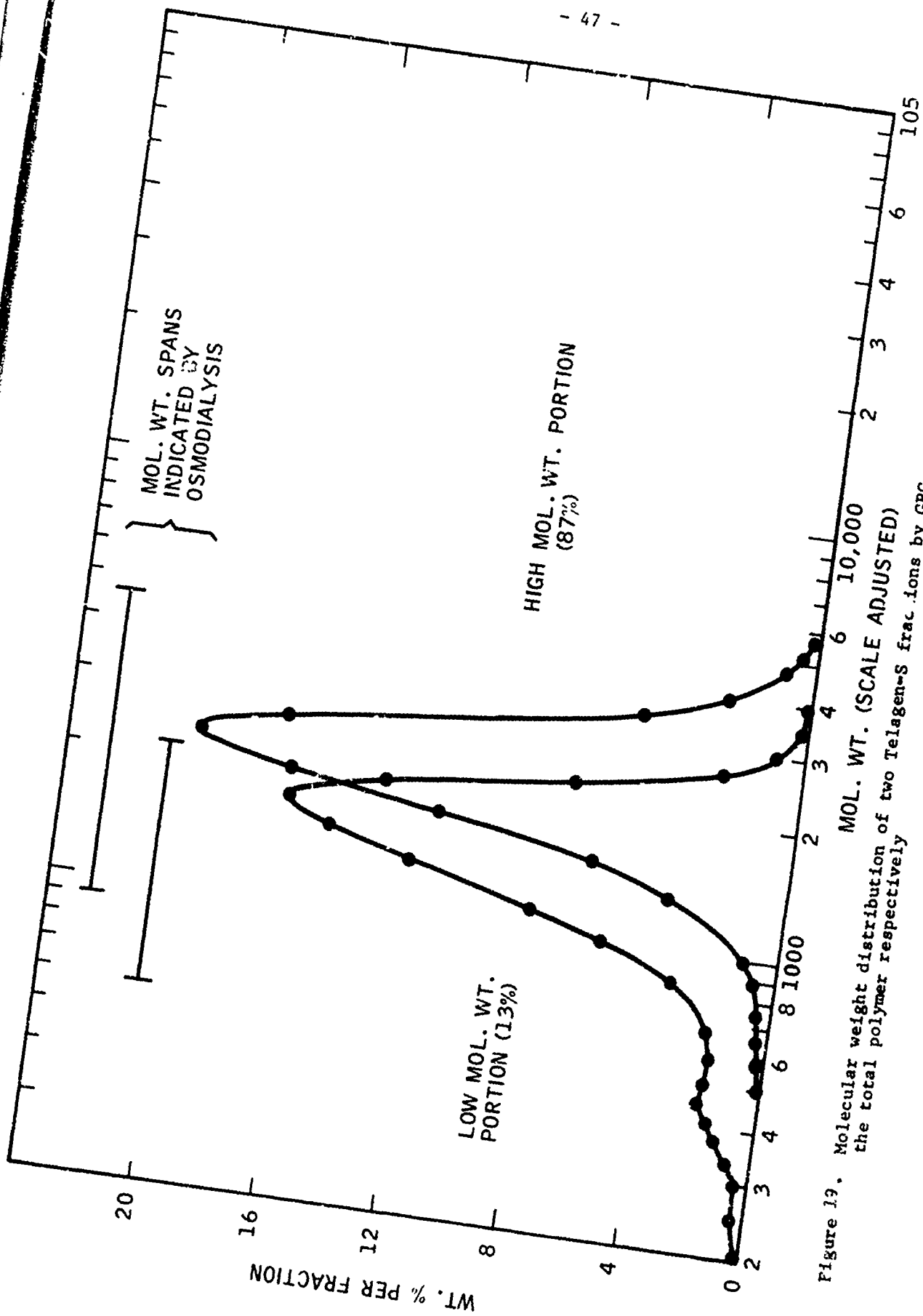


Figure 13. Molecular weight distribution of two Telagen-S fractions by GPC, accounting for 87 and 13 wt.% of the total polymer respectively

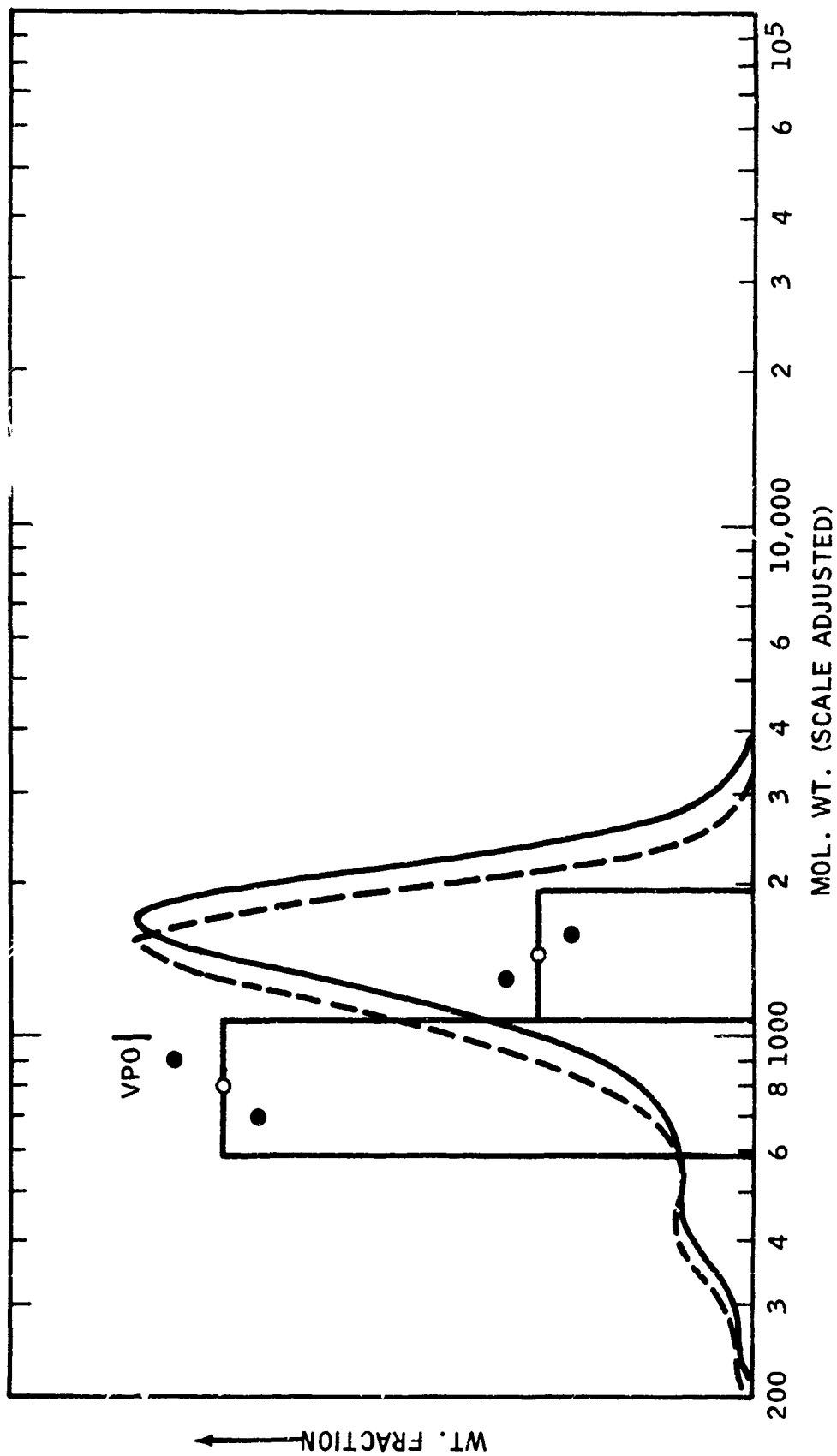


Figure 20. Comparison of molecular weight distribution of the 13 wt.% low molecular weight fraction of Telagen-S by osmodialysis and GPC

In connection with Figure 20, it should be pointed out that the low molecular weights involved lie near the nominal end of the molecular weight scale accessible with the osmodialysis technique and currently employed membranes. Also, it must be remembered that the calibration scheme employed for gel permeation chromatography assumes that all components of Telagen-S will strictly parallel the n-paraffin hydrocarbons in the relationship of elution volume to (log) molecular weight. Nonetheless, examination of histogram and curve of Figure 20 strongly suggests the possibility that the 13% low molecular weight fraction may contain a substantial portion of molecular species sensed by the osmodialysis method but which tend not to be detected by the differential refractometric method employed in GPC.

2. COOH-TELAGEN-S LOT 242 AM-151 BH

COOH-Telagen-S is the hydrogenated, carboxyl-terminated polybutadiene prepared by the General Tire and Rubber Company. It has the same backbone structure as the hydroxyl-terminated Telagen-S. Two different samples of this prepolymer, lot no. 242 AM-151 BH and lot no. 242 Am-194 BH were received from Thiokol, Wasatch Division, for characterization.

The main objective of this characterization is the development of a method for the determination of functionality distribution of COOH-terminated prepolymers. This in turn presupposes that a small scale COOH-equivalent weight method is available to determine the functionality of isolated polymer fractions (50-150 mg). With COOH-terminated prepolymers there is the additional complication arising from the tendency of the carboxyl groups in these polymers to form hydrogen bound aggregates in non-polar solvents. As a result, the number average molecular weight may be too high. The effect of polymer concentration on apparent molecular weight is therefore of particular importance.

The following sections deal with studies of molecular weight, equivalent weight and functionality distribution.

2.1. Molecular Weight Measurements in Benzene and Chloroform

Number average molecular weight measurements of COOH-Telagen-S have been carried out by vapor pressure osmometry (VPO) in two solvent systems, benzene and chloroform. The concentration range extended from about 0.4 to 3.0 wt.% polymer in solution. Figure 21 shows the effect of concentration on the apparent molecular weight, \bar{M}_n . These data allow the following conclusions:

- The COOH-Telagen-S polymer shows a strong concentration dependence of molecular weight. The molecular weight in solution increases with increase in polymer concentration. This trend is in agreement with the reported dimerization of COOH-terminated prepolymers in non-polar and weakly polar solvents such as benzene and chloroform.
- It is interesting that the apparent molecular weight of COOH-Telagen-S is the same in both solvents. This indicates that the same extent of association exists in both solvents.
- These data allow some qualitative estimate of the extent of association in these solvents. At concentrations above 4 to 5%, the polymer is probably completely associated.
- The extrapolated number average molecular weight in these two solvents is $(\bar{M}_n)_0 = 2370$.

- These data again point out the importance of extrapolating the data to zero concentration. Failure to do so may give an erroneously high molecular weight. For instance, molecular weight determinations at a single concentration (30 g/Kg) would give a molecular weight of 4000, which is 70% greater than the correct molecular weight obtained by extrapolation of the data to zero concentration.

Thiokol has reported a number average molecular weight of 2515 for this polymer based on GPC studies.

Molecular weight measurements were also attempted in 1,2 dichloroethane. However, the COOH-Telagen-S polymer was not sufficiently soluble in this solvent to obtain meaningful data.

2.2. Equivalent Weight Measurements

The COOH-equivalent weight of this polymer reported by Thiokol is 0.061 COOH equiv./100 grams which corresponds to 1640 grams/mole COOH. Thiokol determined the equivalent weight by titration in toluene with 0.1 N alcoholic KOH to a phenolphthalein end point.

Equivalent Weight Determination by Potentiometric Titration

We have carried out equivalent weight measurements by potentiometric titration of an MEK solution of the polymer with 0.1 N tetrabutyl ammonium hydroxide in methanol. The results of three determinations are summarized below:

COOH-Equivalent Weight (grams/mole COOH)

1598
1599
1594
1597

The difference between our results and those reported by Thiokol is 2.6%.

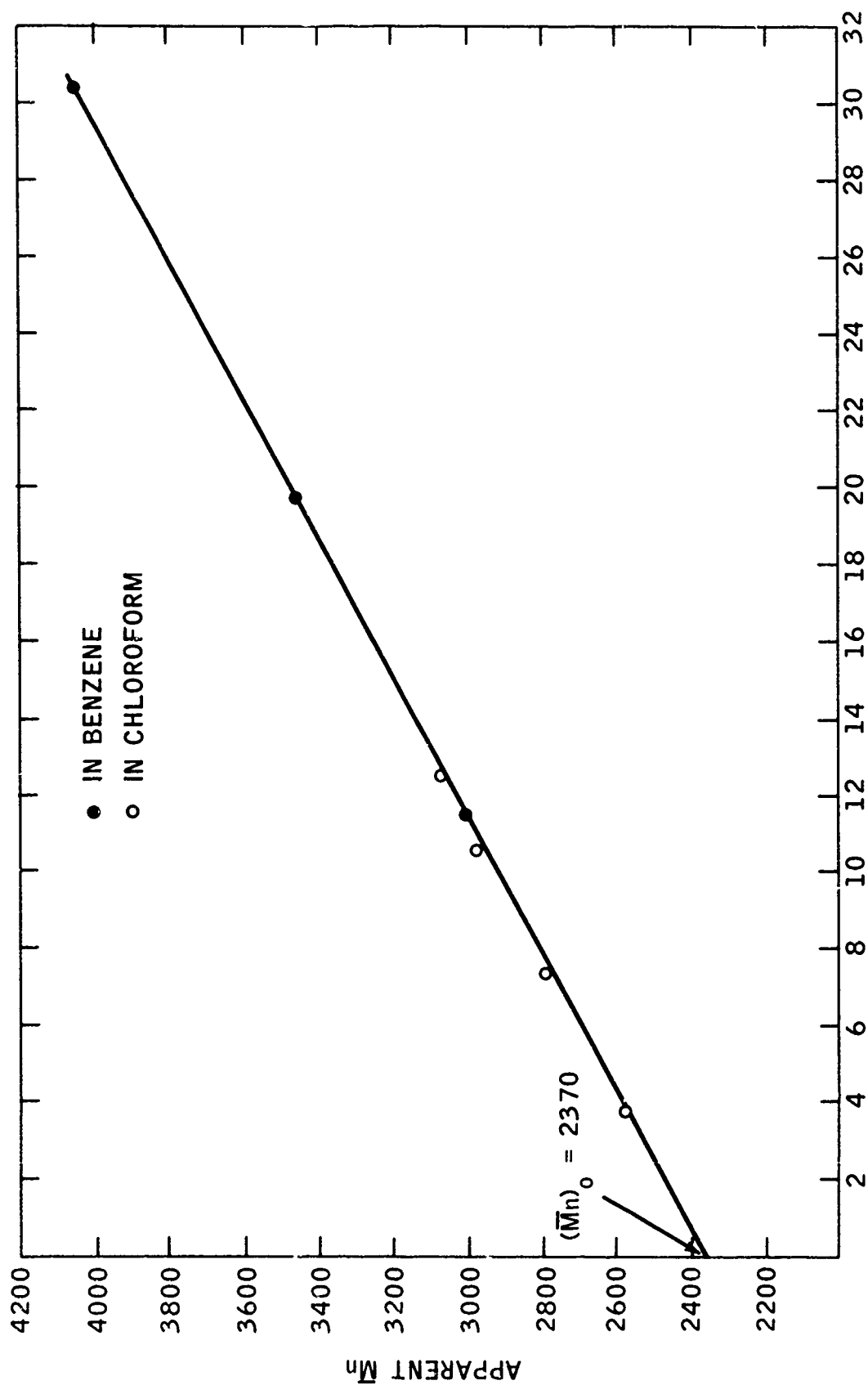


Figure 21. Dependence of apparent molecular weight (\bar{M}_n) on concentration for COOH-Telagen-S, 242 AM 151 BH in benzene and chloroform at 37°C

Equivalent Weight Determination
by Infrared Absorption Measurements

When fractionating polymers by molecular weight or functionality, small polymer fractions are collected which need to be characterized with respect to molecular weight and equivalent weight. A small-scale equivalent weight method is therefore needed which can accurately determine the equivalent weight of 50-100 mg polymer fractions. The acid titration requires substantially larger polymer samples for analysis. The method we are using is similar to the one established for the equivalent weight determination of OH-terminated prepolymers. It is based on measuring the intensity of the carbonyl absorption in the infrared (5.78μ). The method is nondestructive and samples can therefore be recovered for additional characterization such as molecular weight determination. The polymer is dissolved in a polar solvent such as tetrahydrofuran to provide polymer-solvent hydrogen bonding and to avoid polymer-polymer association.

In order to determine the equivalent weight of COOH-terminated polymers, a calibration is needed which relates the intensity of the carbonyl absorption band to the molar concentration of the calibrant. We have chosen stearic acid, a C_{18} organic acid, as the calibrant. The calibration shown in Figure 22 was determined with the aid of a Beckman IR-8. The COOH absorbance of stearic acid solutions in THF was measured at 5.78μ as a function of solute concentration.

Matched cells of 0.103 mm thickness were used to measure the intensity of the absorbance. A background correction was measured by drawing a base line between 5.5μ and 6.3μ .

Results from the infrared absorption method are in good agreement with those obtained by potentiometric titration. COOH-absorption measurements of COOH-Telagen-S have yielded the following results:

COOH-Equivalent Weight by IR
(grams/mole COOH)

1620
1610

1615

This value agrees within 1% of the equivalent weight obtained by acid titration (1597) and differs from Thiokol's results by 1.5%.

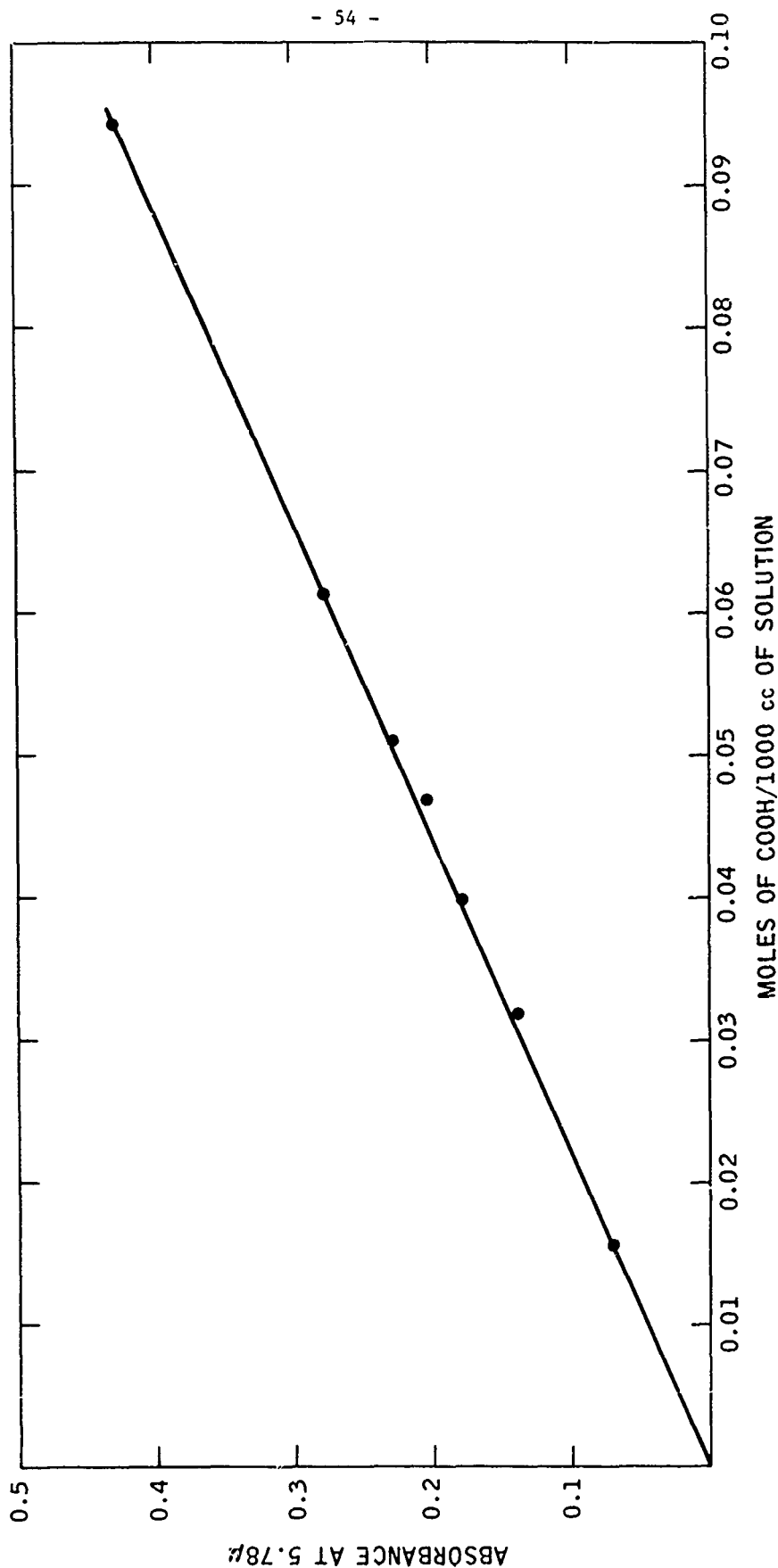


Figure 22. COOH-calibration: stearic acid in tetrahydrofuran, Beckman IR-8, using matched liquid absorption cell, of 0.103 mm thickness

2.3. Functionality of COOH-Telagen-S

Based on molecular weight measurements in benzene and chloroform and equivalent weight measurements by infrared and potentiometric titration, the functionality of COOH-Telagen-S, 242 AM 151 BH is:

$$f = \frac{(\overline{Mn})_0}{\text{Eq. Wt.}} = \frac{2370}{1615} \text{ to } \frac{2370}{1597}$$

$$f = 1.47 \text{ to } 1.48$$

This value suggests that this polymer contains significant fractions of non and/or monofunctional components. The following section describes results on the functionality distribution of COOH-Telagen-S.

2.4. Functionality Distribution

We have carried out some exploratory studies to adapt the functionality distribution method developed for the OH-terminated Telagen-S to the COOH-terminated prepolymer. Our preliminary results indicated that the difunctional COOH-terminated Telagen-S is more strongly adsorbed on silica gel than the difunctional OH-terminated Telagen-S. For instance, the difunctional OH-terminated polymer can be desorbed by $\text{CHCl}_3/\text{CH}_3\text{CN}$ mixtures whereas the difunctional COOH-analogue requires a more polar solvent combination, $\text{CHCl}_3/\text{CH}_3\text{CH}_2\text{OH}$.

The technique is similar to that reported previously for the OH-terminated Telagen-S: a slurry of silica gel in 100% CCl_4 is charged to the column. The polymer is placed on the column in an approximate 20 wt.% solution in CCl_4 . The polymer is then eluted from the column by stepwise addition of CCl_4 , and solvent mixtures of $\text{CCl}_4/\text{CHCl}_3$ and $\text{CHCl}_3/\text{CH}_3\text{CH}_2\text{OH}$. The eluting solvent was collected in 40 ml fractions. All fractions are subsequently stripped to constant weight under vacuum at 40-50°C. Based on the elution profile, the small individual fractions are combined into major fractions. These major fractions are stripped again to constant weight and characterized.

The elution profile of the first fractionation run, 369-95, is shown in Figure 23. The profile indicated essentially three major peaks. The individual fractions were correspondingly combined into three major fractions, representing 10.2, 17.25 and 42.7% of the polymer charged to the column. Total polymer recovery was only 70.15%. Because of sample size limitation, we have obtained only equivalent weight measurements. These data are summarized in the table below.

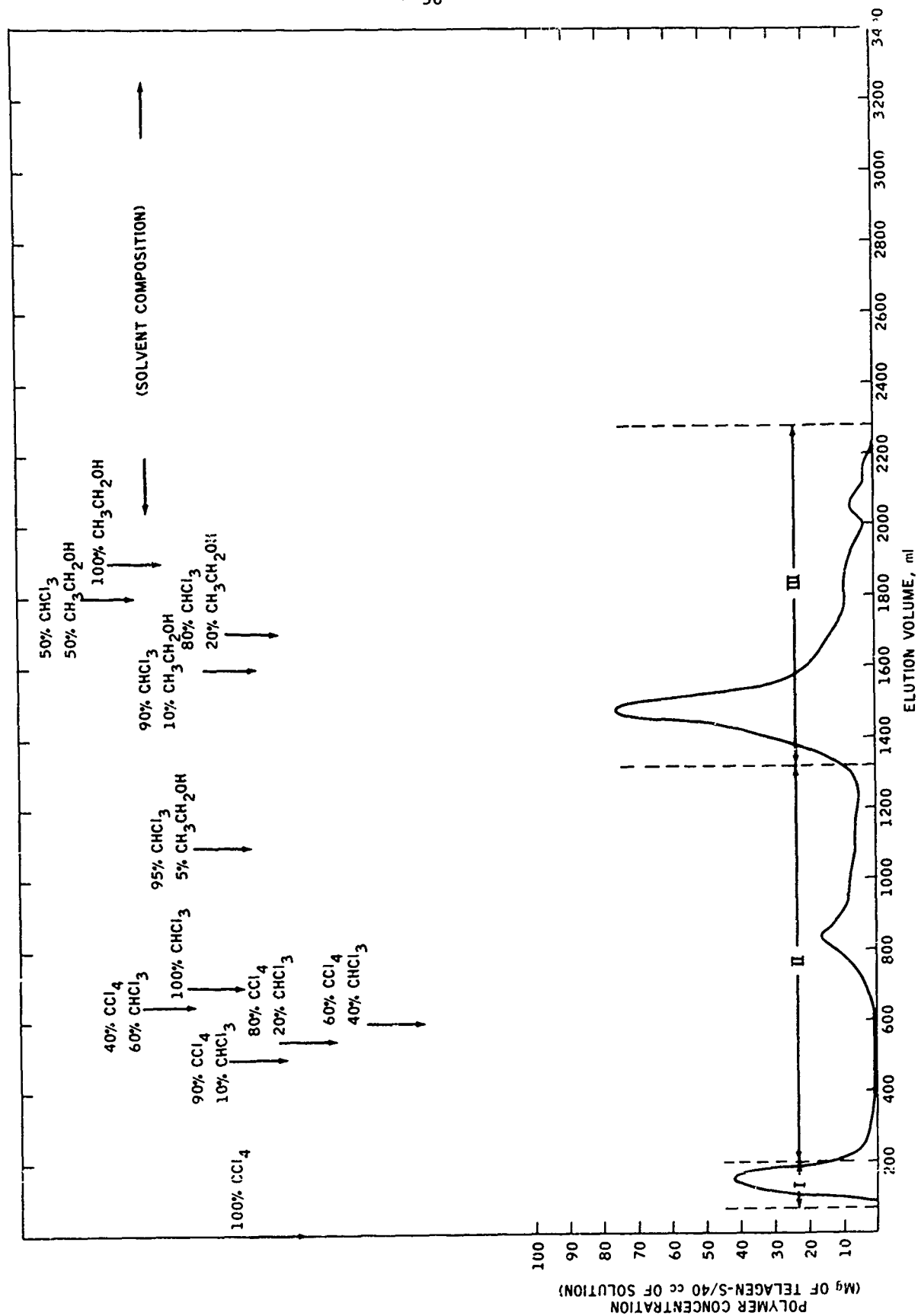


Figure 23. Fractionation of COOH-terminated Telagen-S, 242 AM 151 BH by stepwise elution from silica gel; elution profile of run 369-95. Silica gel/polymer ratio = 115/1

Fractionation of COOH-Telagen-S, 242 AM 151 BH
by Stepwise Elution from Silica Gel

Identification: 369-95
Silica gel/polymer ratio: 115/1
Polymer charged to column: 0.881 g
Total polymer recovery: 70.15%

<u>Fraction</u>	<u>Wt.% of Total</u>	<u>Equivalent Weight (grams/mole COOH)</u>	<u>Remarks</u>
I	10.2	7000	Colorless
II	17.25	3095	Yellow
III	42.7	1370	Reddish-brown

There were distinct differences in the color of these fractions as indicated in the table varying from colorless to reddish-brown.

The elution profile indicated a rather sharp separation between fractions I and II. It was therefore anticipated that fraction I was entirely nonfunctional. Equivalent weight measurements (7000 grams/mole of COOH), however, showed that this fraction contained in part functional components. We believe that this incomplete separation between non- and monofunctional components is a result of dimerization in CCl_4 , the solvent in which the polymer is charged to the column. Association of two monofunctional chains in CCl_4 will result in an apparently "nonfunctional" chain which will not be adsorbed by the silica gel and hence be eluted together with the truly nonfunctional components.

Since fractionation run 369-95 gave poor polymer recovery (70.15%), our main concern was to improve the recovery in subsequent fractionations. Our general experience has been that poor polymer recovery is associated with the formation of hot spots on the column. In fractionation run 369-97 we have therefore increased the ethanol concentration stepwise by small increments from 1.0, 2.0, 3.5 to a concentration of 5%. We have thus effectively eliminated exotherms on the column. As a result, polymer recovery was increased to 96.5%. The results of fractionation run 369-97 are summarized in the table below and the elution profile is shown in Figure 24.

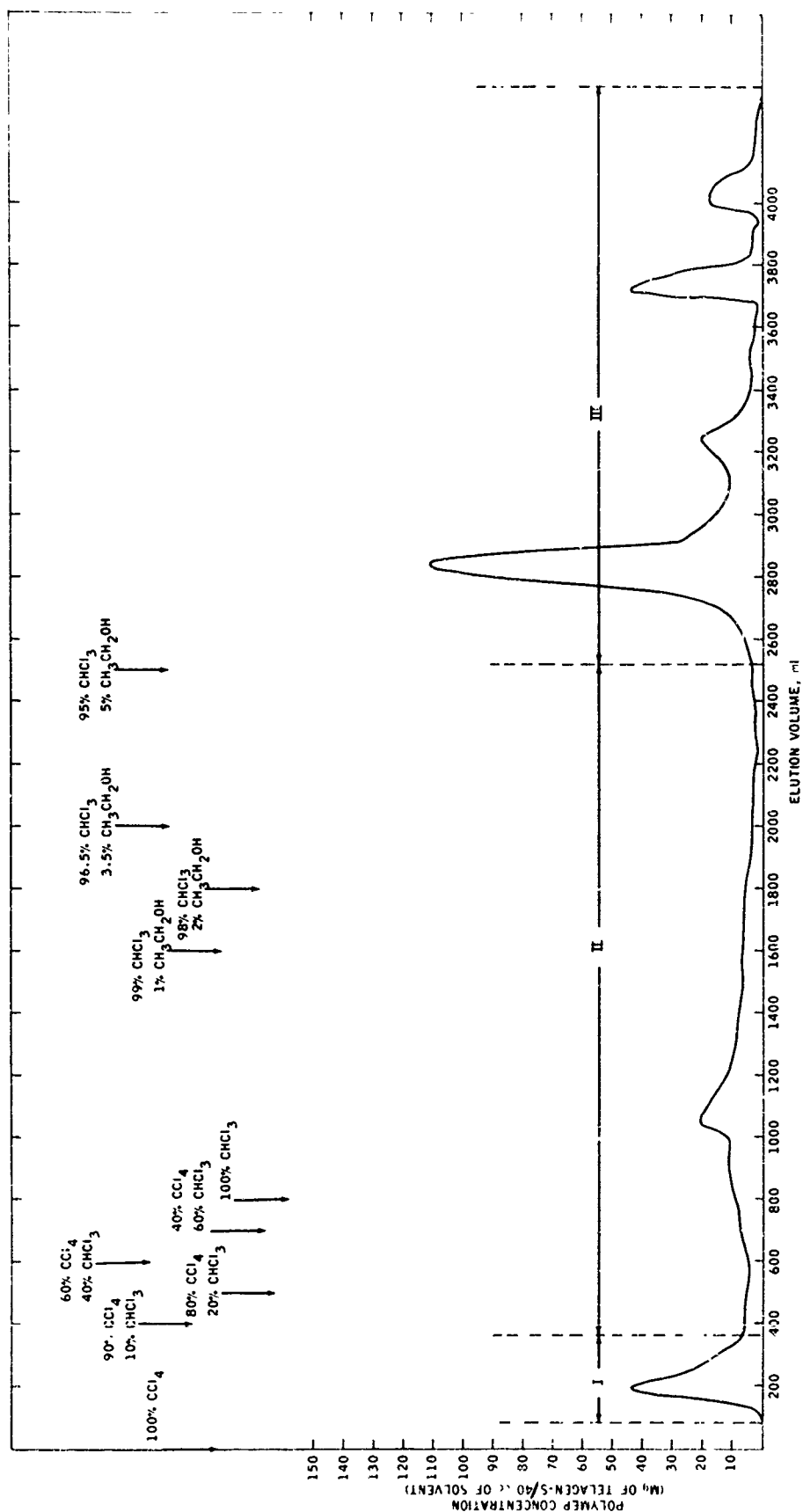


Figure 24. Fractionation of COOH-terminated Telagen-S, 242 AM 151 BH by stepwise elution from silica gel; elution profile of run 369-97. Silica gel/polymer ratio = 100/1

Identification: 369-97
 Silica gel/polymer ratio: 100/1
 Polymer charged to column: 1.258 g
 Total polymer recovery: 96.5%

<u>Fraction</u>	<u>Wt.% of Total</u>	<u>(\bar{M}_n)_o</u>	<u>Equivalent Weight (grams/mole COOH)</u>	<u>Functionality</u>
I	10.8	2550 \pm 100	6500	0.39
II	28.5	3000 \pm 100	3100	0.97
III	57.2	3000 \pm 100	1515	1.98

Analysis of fraction I again indicated incomplete separation of non- and monofunctional components. The overall functionality of this fraction which accounts for 10.8% of the total polymer is 0.39. Since the succeeding fraction is monofunctional, fraction I must be a mixture of non- and monofunctional components. The approximate composition of fraction I based on its overall functionality of 0.39 is 4.2% monofunctional and 6.6% nonfunctional Telagen-S. The total amount of monofunctional Telagen-S is therefore $4.2 + 28.5 \approx 33\%$. Fraction III was found to be difunctional.

When combining the individual cuts comprising fraction II, it was observed that two of the cuts contained a solid component which had separated from the polymer. We believe this material to be antioxidant and therefore did not include these cuts in the combined fraction II.

Reproducibility Check of the Functionality
Distribution by Stepwise Elution from Silica Gel

Preliminary data on the functionality distribution of Lot 242 AM-151 BH had been determined by column chromatography on silica gel. Since this was the first time that we had applied this technique to a COOH-terminated prepolymer, we felt it necessary to carry out one additional fractionation to check the reproducibility of this method. The elution profile (shown in Figure 25) of this most recent fractionation is similar to Run 369-97. The double peak in fraction III was a result of weekend shutdown of the column. The column had been turned off after 3280 ml of solution had been collected. During the weekend shutdown more polymer was desorbed from the gel which was subsequently eluted from the column upon restart. Since only difunctional polymer was left on the column at this point, shutdown of the column did not interfere with the intended fractionation by functionality.

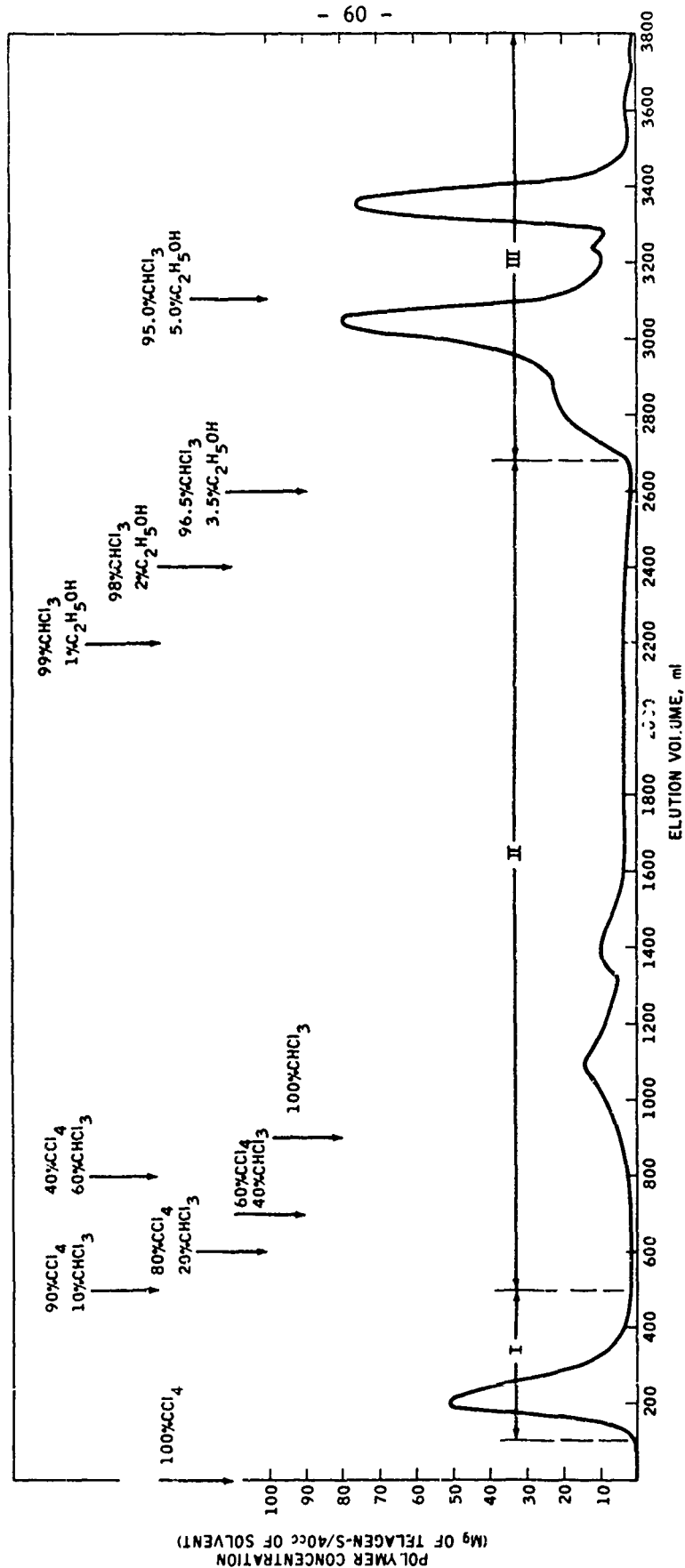


Figure 25. Fractionation of COOH-terminated Telagen-S, 242 AM 151 BH by stepwise elution from silica gel; elution profile of Run 369-111. Silica gel/polymer ratio = 118/1

The results of this latest fractionation are summarized below:

Identification: 369-111
 Silica gel/polymer ratio: 118/1
 Polymer charged to column: 1.102 g
 Total polymer recovery: 95.6%

<u>Fraction</u>	<u>Wt.% of Total</u>	<u>\bar{M}_n</u>	<u>Equivalent Weight (Grams/Mole COOH)</u>	<u>Functionality</u>
I	14.4	2400 \pm 100	5500	0.44
II	24.1	3100 \pm 100	3090	1.0
III	57.1	2900 \pm 100	1490	1.95

Analysis of fraction I again indicates that it is a mixture of non- and monofunctional components. The approximate composition of fraction I based on its overall functionality of 0.44 is about 6.3% monofunctional and 8.1% nonfunctional Telagen-S. Fraction II, which accounts for 24.1% of the total, is strictly monofunctional. Therefore, the total amount of monofunctional material is $24.1 + 6.3 \approx 30\%$. The total amount of non- and monofunctional polymer components is 38.5% which is in good agreement with the results of fractionation Run 369-97 which indicated the presence of 39.3% of non- and monofunctional material.

2.5. Fractionation of COOH-Telagen-S Via the Potassium Salt

The method we have developed for the separation of carboxy-terminated Telagen-S into non-, mono- and difunctional components by stepwise elution from silica gel is an analytical tool and not readily adaptable for large scale separation. We have therefore undertaken a study to explore the possibility of separating non- and monofunctional components from the desired difunctional material by converting the carboxylic acid groups of the polymer to the corresponding potassium salts and subsequently extracting preferentially the dipotassium salts with water. The success of this potential separation method depends on the relative solubilities of the mono- and dipotassium salts in water. Although this technique is not likely to provide a quantitative separation of mono- and difunctional material, it may provide the opportunity of greatly reducing material of low functionality on a relatively large scale.

The scheme employed initially is as follows:

- COOH-Telagen-S is dissolved in hexane.
- Isopropyl alcohol is added and the polymer is neutralized with aqueous KOH to a pH of 11.
- Water is then added to affect phase separation.
- The soap solution is separated from the hexane layer and extracted with fresh hexane.

- Soap solution is treated with HCl to pH of 1. The regenerated acids are extracted with hexane, washed free of HCl, and solvent is stripped to recover acids.
- Similarly, all hexane layers are treated with HCl and stripped free of solvent to recover polymer.

These separation studies were carried out with COOH-Telagen-S, Lot 242 AM 151 BH, which had been shown to contain significant amounts of non- and monofunctional (38-39%) components by fractionation on silica gel. Complete analysis of the fractions isolated is summarized below:

Fractionation of COOH-Telagen-S, 242 AM 151 BH
Via Extraction of the Potassium Salt

Identification: 369-118
Amount of polymer separated: 5 grams
% recovery: 96%

<u>Fraction</u>	<u>% of Total</u>	<u>(\bar{M}_n) *</u>	<u>Equivalent Weight**</u> <u>(Grams/Mole COOH)</u>	<u>Functionality</u>
Residual				
Hydrocarbon Layer	58.0	2520	2290	1.1
Aqueous Layer I	18.0	2000	1010	1.98
Aqueous Layer II	20.0	3040	1615	1.88

* By VPO in chloroform at 37°C.

** By infrared absorption measurements in THF.

The data indicate that material of high functionality is preferentially extracted. For instance, aqueous extract I is strictly difunctional material. The second extract, although significantly higher in functionality than the starting material, obviously contains some material of functionality less than two. The remaining hydrocarbon layer (58%) contains the bulk of non- and monofunctional material but also includes a significant amount of difunctional material.

The amount of water added to the system is quite critical. Above a certain amount, a stable emulsion forms which does not break even after standing for days. By adding additional isopropyl alcohol to the system, the emulsion breaks and phase separation takes place. The amount of polymer extracted into the aqueous phase depends on the overall polymer concentration and the relative amounts of hexane, isopropyl alcohol and water used.

A second fractionation run was carried out extracting a total of 46.2% of the polymer. The results are summarized below.

Identification: 369-120
Amount of polymer separated: 3 grams
% of recovery: 95.7%

<u>Fraction</u>	<u>% of Total</u>	<u>\bar{M}_n</u>	<u>Equivalent Weight (Grams/Mole COOH)</u>	<u>Functionality</u>
Residual				
Hydrocarbon Layer	49.5	2810	1975	1.42
Aqueous Layer I	38.4	2840	1500	1.89
Aqueous Layer II	7.8	2900	1770	1.64

The amount of polymer extracted in the first aqueous layer was doubled (38.4 vs. 18%). However, analysis shows that this fraction is no longer strictly difunctional. Subsequent extracts (aqueous layer II) have progressively lower functionality.

A detailed study of the parameters affecting selective extraction might establish more optimum conditions. To date, however, the method is not selective enough to permit quantitative separation of difunctional prepolymer from the non- and monofunctional components.

3. COOH-TELAGEN-S, LOT 242 AM-194 BH

This second sample of COOH-Telagen-S, designated lot 242 AM-194 BH was lighter in color and apparently of lower viscosity than the lot 242 AM-151 BH. As shown by subsequent functionality and functionality distribution measurements, lot 194 BH had significantly higher functionality.

3.1. Molecular Weight Measurements by VPO in Chloroform and Dichlorobenzene

Number average molecular weight measurements of this latest lot of COOH-Telagen-S have been carried out by vapor pressure osmometry (VPO) in two solvents (chloroform and o-dichlorobenzene) at different temperature levels. Measurements in chloroform were carried out at 37°C using benzil as the calibrant. Molecular weight determinations in o-dichlorobenzene were made at 130°C using tetracosane as the calibrant. The concentration range extended from about 0.4 to 2.7 wt.% polymer in solution. Figure 26 shows the effect of concentration on the apparent molecular weight, \bar{M}_n . The extrapolated molecular weights $(\bar{M}_n)_0$ in the two solvent-temperature systems were calculated by a least square analysis of the data. Although these measurements were carried out in two different VPO instruments, using different solvent systems, temperatures and calibrants, the extrapolated molecular weights $(\bar{M}_n)_0$ are in excellent agreement.

$(\bar{M}_n)_0$ in Chloroform at 37°C	$(\bar{M}_n)_0$ in o-Dichlorobenzene at 130°C
2380	2340
% $\Delta (\bar{M}_n)_0 = 1.7\%$	
Average $(\bar{M}_n)_0 = 2360$	

Figure 26 shows again the strong concentration dependence of molecular weight in chloroform at 37°C. In contrast molecular weight measurements in o-dichlorobenzene at 130°C show only a slight concentration dependence. The lower concentration dependence in o-dichlorobenzene at 130°C probably reflects the effect of higher temperature on polymer association in solution which tends to reduce the degree of dimerization. These data point out that when molecular weight measurements are made at a single concentration (and hence extrapolation to zero concentration is not possible) it is important that these measurements are made at high temperatures (130°C) where the concentration dependence of molecular weight is minimized. Otherwise serious errors might result from the failure to extrapolate to zero concentration.

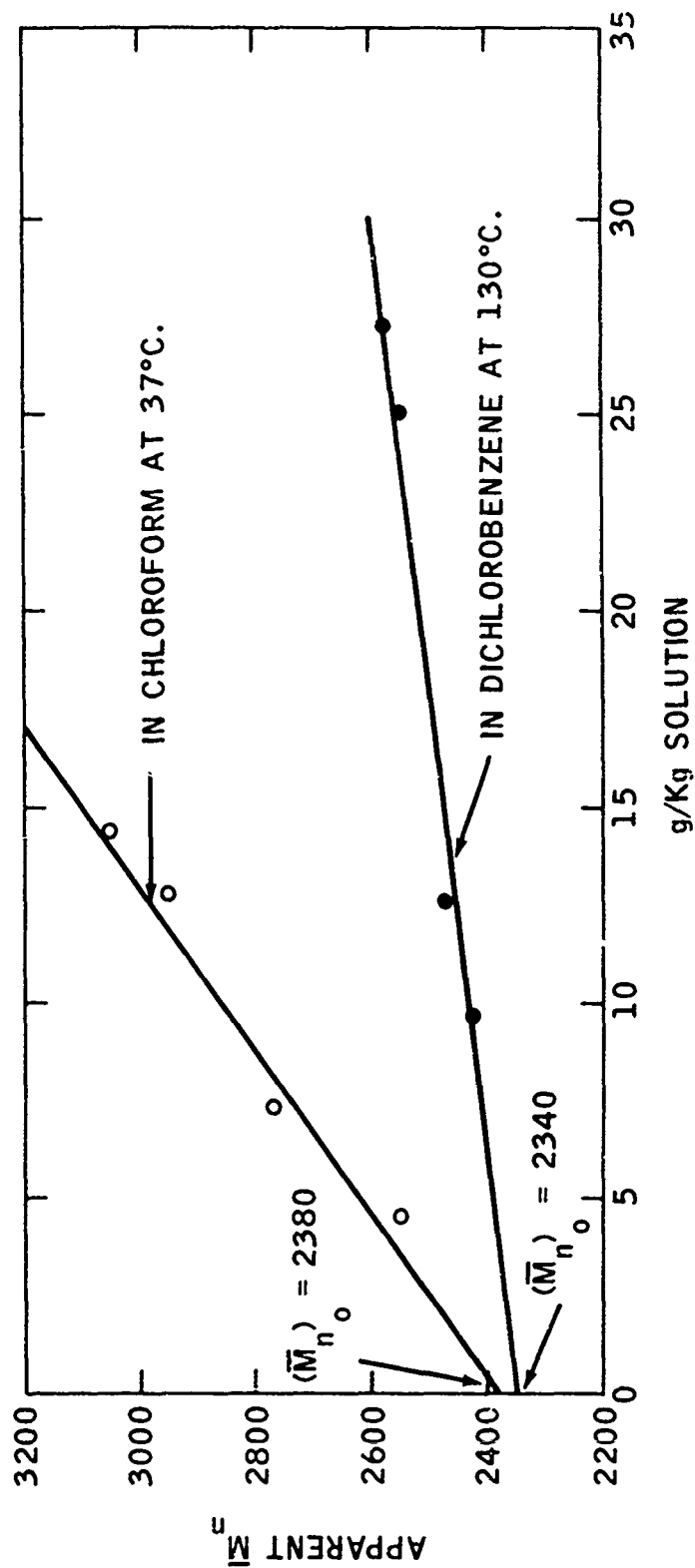


Figure 26. Concentration dependence of molecular weight for COOH-Telagen-S, 242 AM 194 BH in chloroform at 37°C and o-dichlorobenzene at 130°C

Tetrahydrofuran as a Solvent
for Use in VPO Measurements

We have investigated tetrahydrofuran as a potential solvent for molecular weight determinations by vapor pressure osmometry at 37°C. Using chromatography tetrahydrofuran, the ΔR reading for solvent vs. solvent (ΔR_{ss}) was found to be nonreproducible and exhibited great variations with time. No valid calibration curve could therefore be established for benzil in this solvent. A similar difficulty has been reported by the Thiokol Chemical Corporation, Elkton Division (2).

3.2. Equivalent Weight Determination by Potentiometric
Titration and Infrared Absorption Measurements

The COOH-equivalent weight was determined by (1) potentiometric titration with 0.1 N tetrabutyl ammonium hydroxide and by (2) infrared absorption measurements at 5.8 μ . The results of these determinations are summarized below:

<u>COOH-Equivalent Weight (Grams/Mole COOH)</u>	
by	
<u>Potentiometric Titration with 0.1 N Tetrabutyl Ammonium Hydroxide</u>	<u>Infrared Absorption Measurements at 5.8μ</u>
1357	1390
1360	1390
1361	1360
	<u>1380</u>
Average: 1359	Average: 1390

The difference between these average values is 1.5%.

(2) Advanced Binder Synthesis, Interim 12-Months Report, September 1967.

3.3. Functionality

Based on molecular weight measurements in chloroform and o-dichlorobenzene and equivalent weight measurements by potentiometric titration and infrared measurements, the overall functionality of COOH-Telagen-S 242 AM 194 BH is:

$$f = \frac{(\bar{M}_n)_o}{\text{Eq. Wt.}} = \frac{2360}{1370} = 1.72$$

The functionality of Lot 242 AM 194 BH is significantly higher than that of Lot 242 AM 151 BH which had previously been determined ($f = 1.48$). Nevertheless, the functionality of 1.72 suggested that this latest lot contained non- and monofunctional components. Fractionation by stepwise elution from silica gel as discussed in the following section confirmed the presence of non- and monofunctional components.

3.4. Functionality Distribution

COOH-Telagen-S, Lot 242 AM 194 BH, was fractionated by stepwise elution from silica gel to determine its functionality distribution. Figure 27 shows the characteristic elution profile of carboxy-terminated Telagen-S. Based on the elution profile, the individual cuts were appropriately combined into three main fractions. The results of this fractionation and analysis of the fractions are summarized below:

Identification:	369-116
Silica gel/polymer ratio:	100/1
Polymer charged to column:	1.316 g
Total polymer recovery:	92.2%

<u>Fraction</u>	<u>Wt.% of Total</u>	<u>$(\bar{M}_n)_o$ *</u>	<u>Equivalent Weight** (Grams/Mole COOH)</u>	<u>Functionality</u>
I	3.3	***	8200	
II	15.3	2850	2830	1.0
III	73.6	2620	1318	1.99

* Molecular weight measurements were carried out in chloroform at 37°C. $(\bar{M}_n)_o$ was calculated by least square analysis of the data.

** By infrared absorption measurements.

*** Limited sample size did not permit molecular weight measurements.

It is quite obvious from the analysis that Lot 242 AM 194 BH contains considerably less non- and monofunctional components than Lot 242 AM 151 BH which had previously been characterized. The total amount of non- and monofunctional polymer components (fractions I and II) account for only 18.6% of the total polymer. Because of sample size limitation (fraction I contained only 43 mg), molecular weight measurements could not be obtained on fraction I. Equivalent weight measurement of fraction I, however, indicates that the bulk of this fraction is nonfunctional. An estimated breakdown of fraction I is about 2.5% nonfunctional and 0.8% monofunctional. Fraction II, which accounts for 15.3% of the total, is strictly monofunctional. Therefore, the total amount of monofunctional material is about 16%. Fraction III is difunctional. These fractionation results confirm that Lot 242 AM 194 BH represents a considerable improvement in functionality as compared to Lot 242 AM 151 BH previously submitted for analysis by Thiokol.

The concentration dependence of molecular weight of mono- and difunctional COOH-Telagen-S in chloroform at 37°C is shown in Figure 28. The difunctional prepolymer shows considerably greater concentration dependence of molecular weight than the monofunctional analogue. The tendency for polymer-polymer association in chloroform is obviously considerably greater for the difunctional COOH-Telagen-S. Figure 28 permits a quantitative estimate of the relative association of mono- and difunctional carboxy-terminated Telagen-S in chloroform.

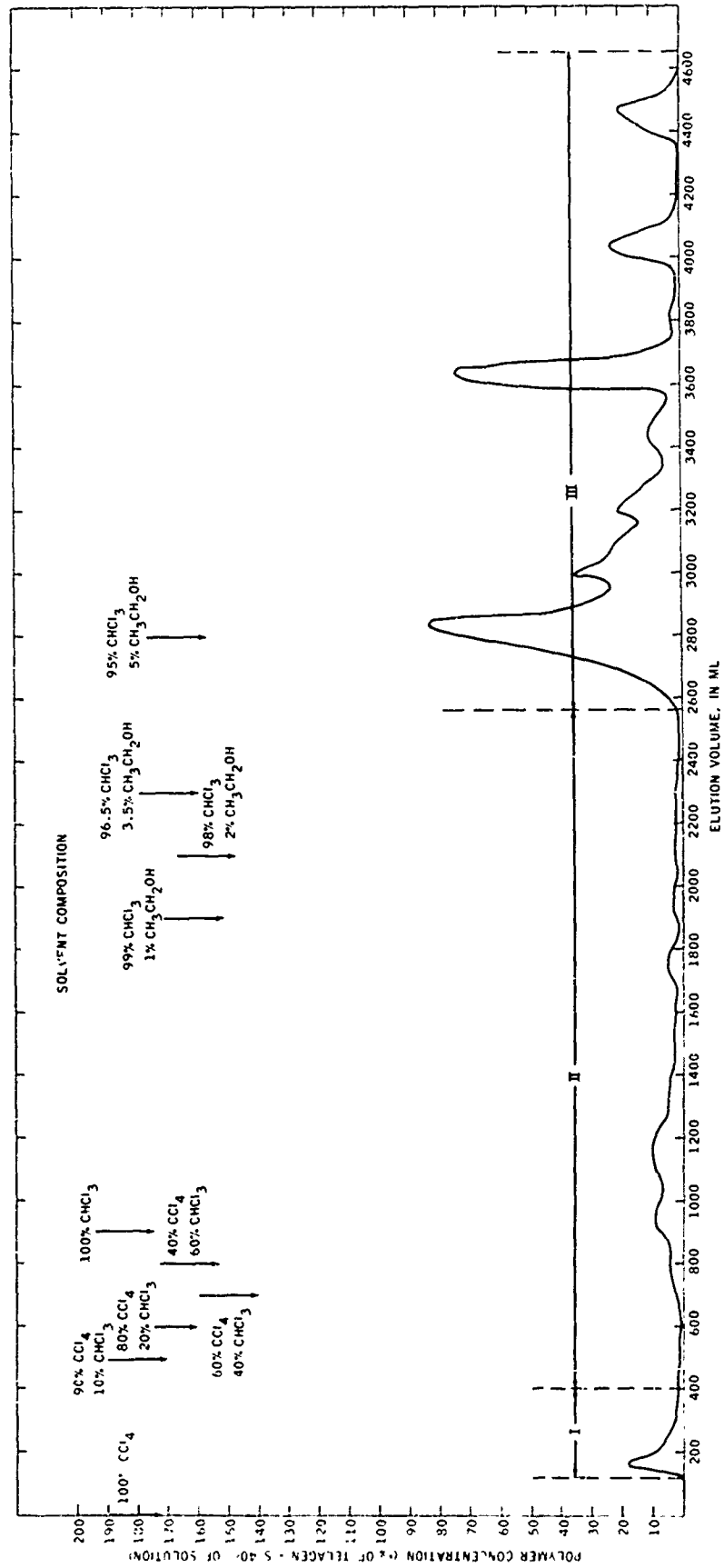


Figure 27. Fractionation of COOH-Telagen-S, 242 AM 194 BH by stepwise elution from silica gel; elution profile of run 369-116. Silica gel/polymer ratio = 100/1

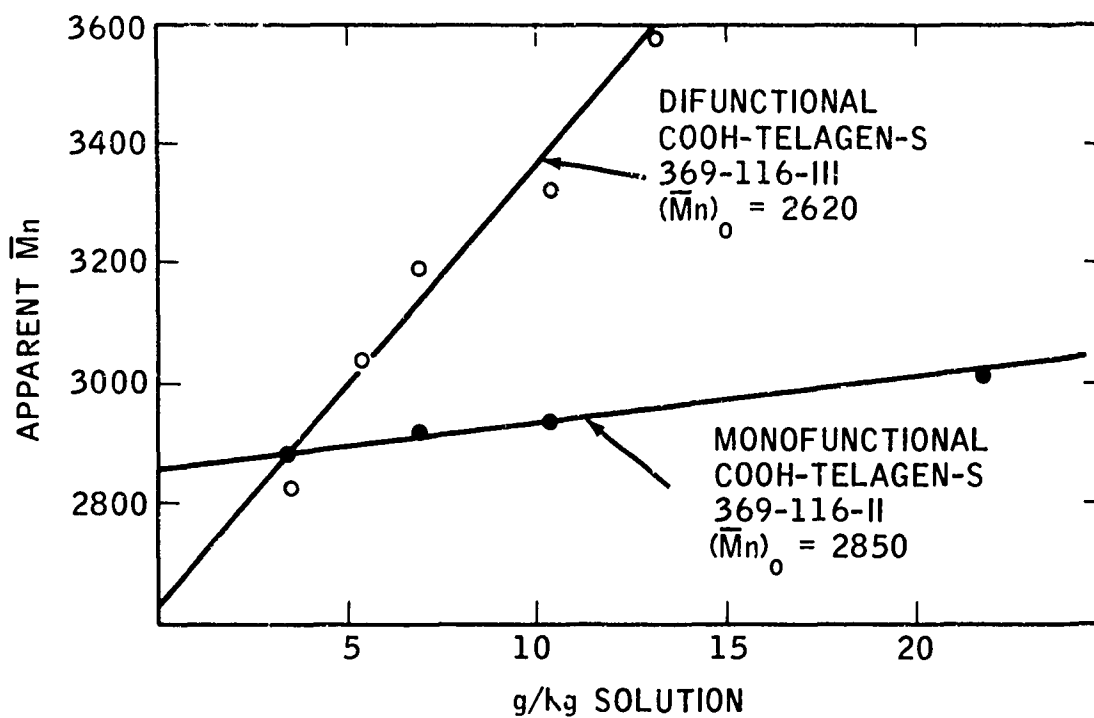


Figure 28. Concentration dependence of molecular weight for mono- and difunctional COOH-Telagen-S in chloroform at 37°C

4. COOH-POLYISOBUTYLENE, EMD-590

A 10 lb batch of carboxy-terminated polyisobutylene designated EMD-590, lot CP₃-21-1 was submitted by the Enjay Polymer Laboratories to the Air Force Rocket Propulsion Laboratory, Edwards Air Force Base for in-house evaluation. We have characterized this prepolymer with respect to molecular weight, equivalent weight, functionality and functionality distribution.

4.1. Molecular Weight Measurements by VPO in Dichlorobenzene at 130°C

Number average molecular weight measurements of the carboxy-terminated polyisobutylene were carried out by VPO in o-dichlorobenzene at 130°C. Previous molecular weight measurements of other carboxy-terminated prepolymers such as COOH-Telagen-S had shown that the concentration dependence of molecular weight for these polymers was minimized in the above solvent-temperature system. Figure 29 shows the effect of concentration on the apparent molecular weight for EMD-590. The molecular weight is essentially independent of concentration in the above solvent-temperature system over the concentration range from 0.5 to 2.0 wt.% polymer. The extrapolated molecular weight $(\bar{M}_n)_0$ is 1920. These data reaffirm our previous contention that molecular weight measurements of carboxy-terminated prepolymers are preferentially made at higher temperatures to greatly reduce or eliminate concentration effects. Caution should be exercised though in considering the thermal stability of prepolymers at this temperature. The temperature level may be too severe for unsaturated prepolymers.

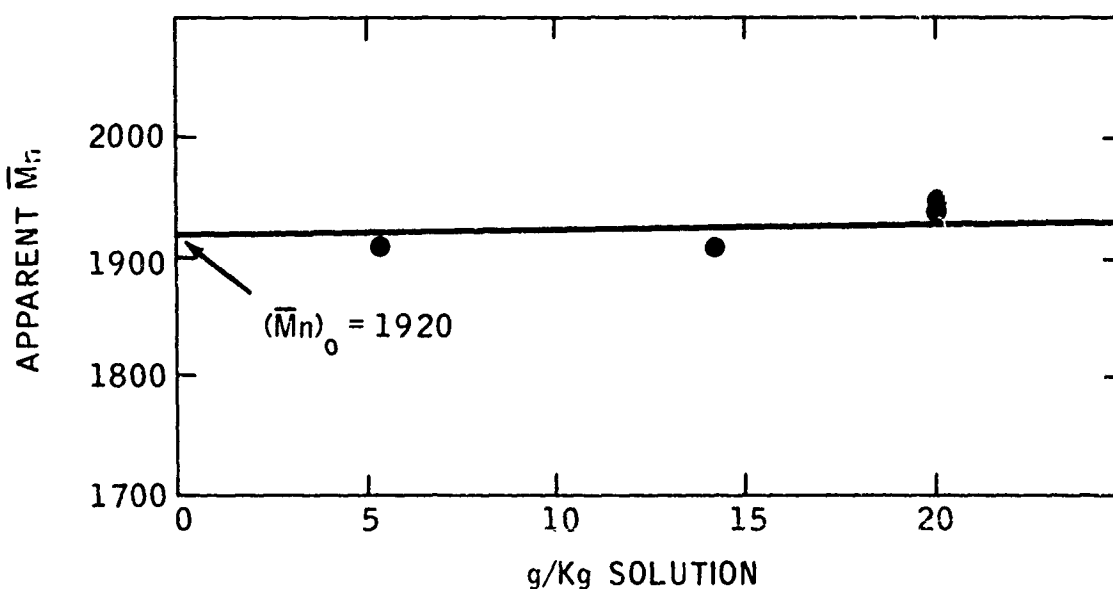


Figure 29. Concentration dependence of molecular weight for COOH-polyisobutylene, EMD-590, Lot CP₃ 21-1 in o-dichlorobenzene at 130°C

4.2. Equivalent Weight Measurements

The COOH-equivalent weight of this prepolymer was determined by the two methods previously employed for COOH-Telagen-S: (1) potentiometric titration and (2) by infrared absorption measurements. The results are summarized below:

COOH-Equivalent Weight (Grams/Mole COOH)	
by	
Potentiometric Titration With 0.1 N Tetrabutyl Ammonium Hydroxide	Infrared Absorption Measurements at 5.8 μ
1092	1115
<u>1089</u>	<u>1105</u>
Average: 1090 g/mole	Average: 1110 g/mole

The difference between these average values is 1.8%.

4.3. Functionality

Based on molecular weight measurements in o-dichlorobenzene and equivalent weight measurements by potentiometric titration and infrared measurements, the overall functionality of the COOH-terminated polyisobutylene, Lot CP 21-1 is:

$$f = \frac{(\bar{M}_n)_o}{\text{Eq. Wt.}} = \frac{1920}{1110} = 1.73$$

$$= \frac{1920}{1090} = 1.76$$

The overall functionality (1.73 to 1.76) of this batch of COOH-polyisobutylene suggests the presence of components having less than theoretical functionality (2). A fractionation by stepwise elution from silica gel was therefore carried out to confirm the presence of mono- and/or nonfunctional components.

4.4. Functionality Distribution

COOH-terminated polyisobutylene, EMD-590, Lot CP 21-1 was fractionated by stepwise elution from silica gel using the procedure previously described for the fractionation of COOH-Telagen-S. Figure 30 shows the elution profile for this polymer. The individual cuts were combined into three fractions based on the shape of the elution profile. The results of this fractionation and analysis of the fractions are summarized below:

Identification: 369-128
 Silica gel/polymer ratio: 118/1
 Polymer charged to column: 1.105 g
 Total polymer recovery: 96.65%

<u>Fraction</u>	<u>Wt.% of Total</u>	<u>\bar{M}_n *</u>	<u>Equivalent Weight** (Grams/Mole COOH)</u>	<u>Functionality</u>
I	1.81***	--	--	--
II	16.83	3300	3340	0.99
III	<u>78.01</u>	2040	1030	1.98
	96.65%			

* Molecular weight measurements were carried out in chloroform at 37°C.

** By infrared absorption measurements.

*** Limited sample size (20 mg) did not permit quantitative analysis of this fraction.

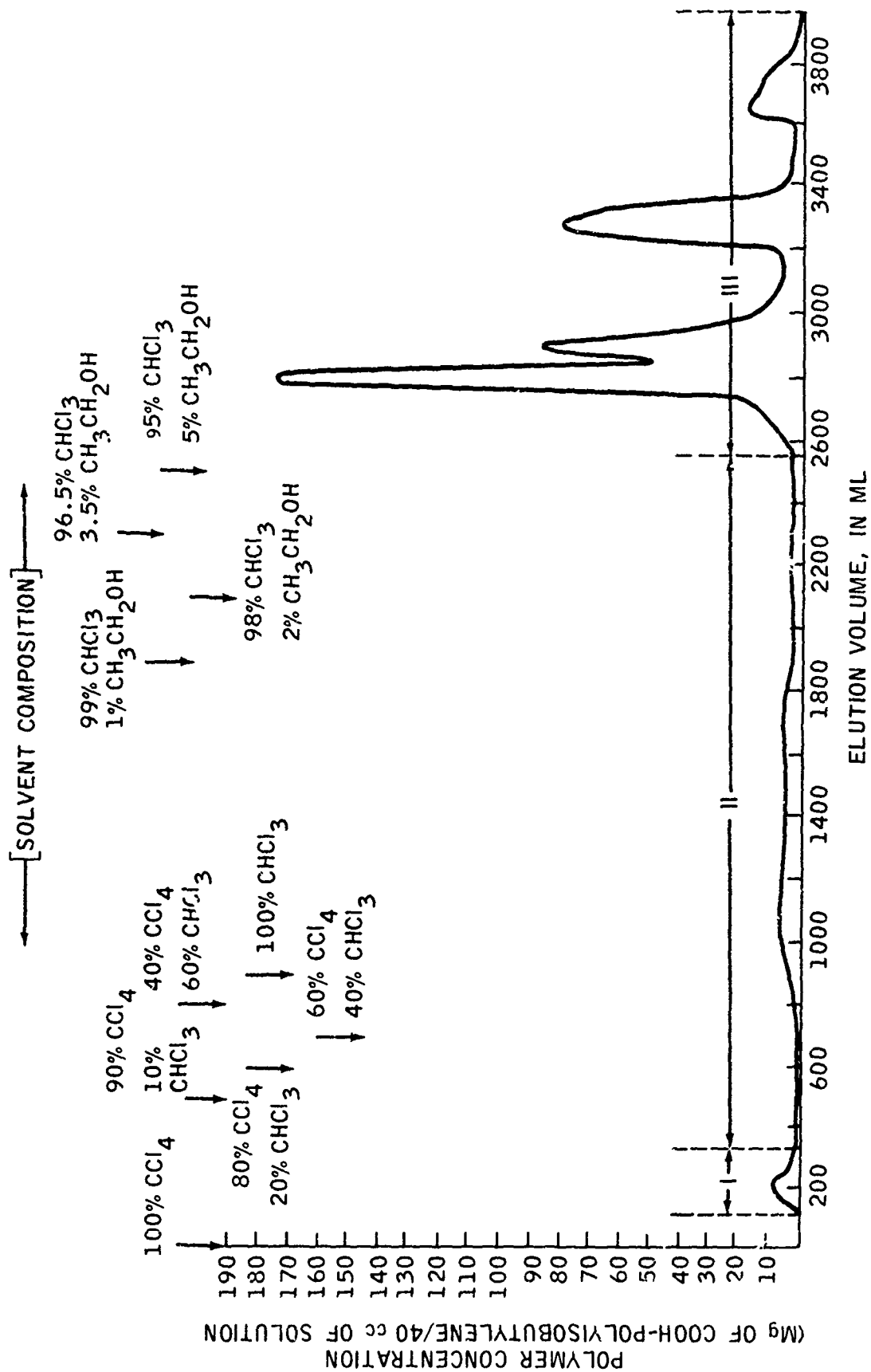


Figure 30. Fractionation of carboxy-terminated polyisobutylene, (CTPIB), EMD-590, Lot CP₃ 21-1 by stepwise elution from silica gel; elution profile of run 369-128. Silica gel/polymer ratio = 118/1

The analyses show that the above fractionation method developed for the Telagen-S prepolymer (saturated polybutadienes) is equally applicable to COOH-terminated polyisobutylene. Fraction I which accounts for 1.8% of the total prepolymer could not be quantitatively analyzed because of sample size limitations (20 mg). However, the infrared spectrum (in Appendix B-4) shows only a minor absorption band at 5.8μ indicating that this fraction is essentially nonfunctional. Fraction II (see Appendix B-4 for infrared spectrum) which accounts for 16.8% of the total polymer is strictly monofunctional ($f = 0.99$). The total amount of non- and monofunctional polymer components is therefore 18.6%. Fraction III, the bulk of the prepolymer is strictly difunctional.

The fact that the two main fractions (II and III) have higher molecular weights than the total polymer before fractionation ($M_n = 1930$) is attributable to the removal of low molecular weight impurities as a result of the fractionation. This same trend has been repeatedly observed when fractionating the COOH-Telagen-S prepolymer.

5. P-BEP, LOT 9088-180A

P-BEP is an energetic, hydroxy-functional prepolymer, being developed by Shell under Contract AF04(611)-8168. Three different lots were received for characterization.

5.1. Molecular Weight Measurements

Molecular weight measurements were carried out by VPO at 37°C in two different solvents, benzene and 1,2-dichloroethane. Figure 31 shows the concentration dependence of the apparent molecular weight in the two solvents. The extrapolated molecular weights to infinite dilution yield closely comparable $(\bar{M}_n)_0$ values (3410 vs. 3470) in the two solvent-calibrant systems. This builds confidence in the absolute accuracy of the VPO method in application to P-BEP.

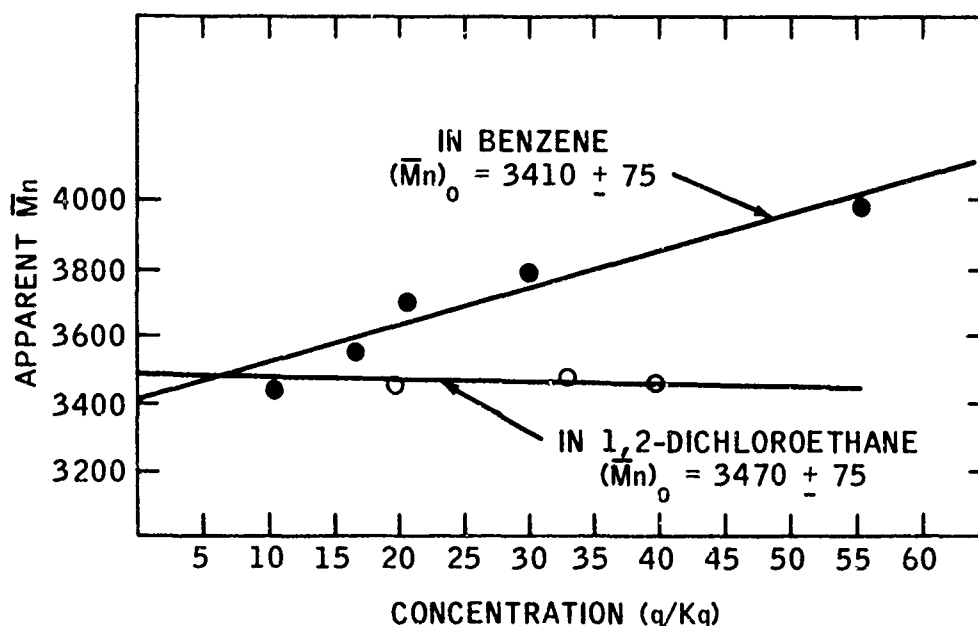


Figure 31. Dependence of apparent molecular weight (\bar{M}_n) on concentration for P-BEP, 9088-180A, in two different solvents at 37°C

In addition to the above molecular weight measurements in benzene and dichloroethane we also investigated a more polar solvent, ethyl acetate. Molecular weight data are shown as a function of concentration with ethyl acetate as solvent (benzil calibrant) in Figure 32 for a low molecular weight P-BEP fraction (SiO₂ gel chromatographed), and in Figure 33 for a higher molecular weight fraction. In both cases, data obtained in dichloroethane are included for comparison. Both the low and high molecular weight P-BEP fractions exhibit a substantial negative dependence of \bar{M}_n (app.) on concentration with ethyl acetate as the solvent. Extrapolated $(\bar{M}_n)_0$ data agree, however, with results obtained in dichloroethane within the overall precision of the method.

Comparative $(\bar{M}_n)_0$ in Two Solvents

	P-BEP Fractions	
	<u>Low Mol. Wt.</u>	<u>High Mol. Wt.</u>
Ethyl acetate	2870	6400
1,2-Dichloroethane	2750	6100
Δ , % (EA/DCE)	+4	+5

The fact that significantly lower $(\bar{M}_n)_0$ were not obtained in the more polar ethyl acetate solvent negates the existence of any measurable interfering effects due to polymer association.

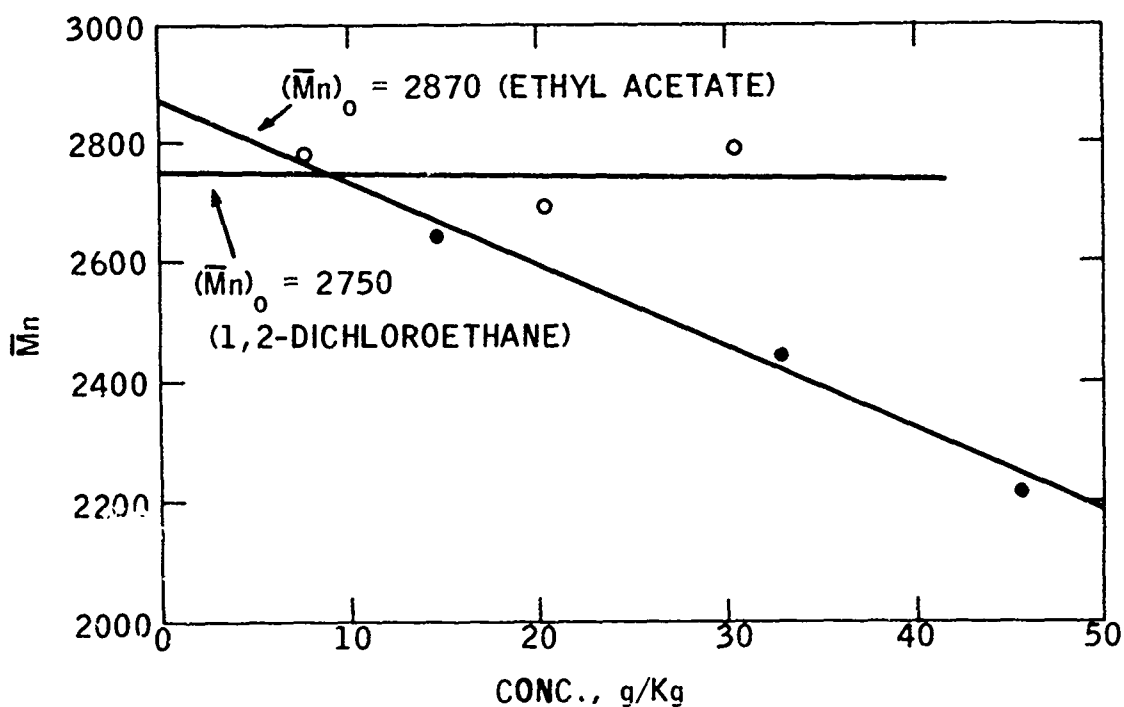


Figure 32. VPO molecular weight measurements at 37°C of low molecular weight P-BEP (fraction 369-58-II) in dichloroethane and in ethyl acetate solvents

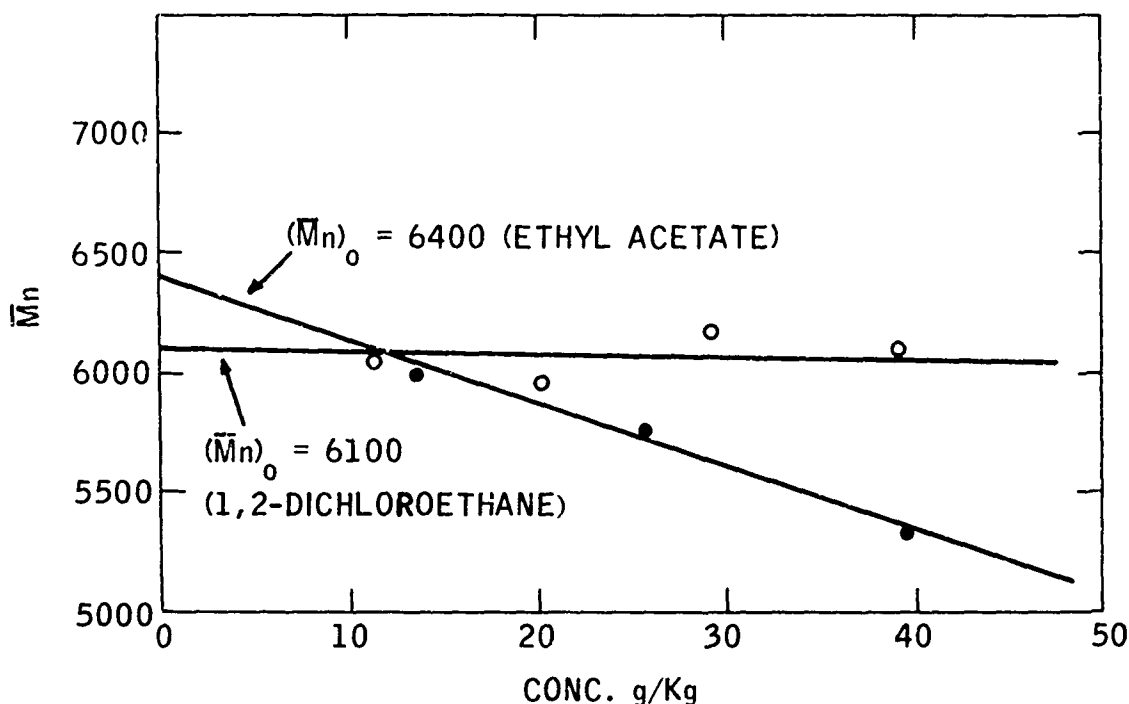


Figure 33. VPO molecular weight measurements at 37°C of high molecular weight P-BEP (fraction 369-58-I) in dichloroethane and in ethyl acetate solvents

5.2. Equivalent Weight Measurements

(a) Infrared Absorption Measurements

Similarly to the work described on OH-Telagen-S, we have established an infrared calibration for determining the OH-equivalent weight of P-BEP on the basis of n-butanol reference blends in methyl ethyl ketone. The methyl ethyl ketone that was used as the solvent was dried with silica gel and subsequently stored over 4A molecular sieve. The calibration was determined with the aid of a Beckman IR-8. OH absorbance was measured at 2.82 microns as a function of solution concentration in the case of the n-butanol reference blends. For P-BEP solutions the maximum absorption was shifted to 2.85 μ . A 0.1055 mm thick liquid absorption cell was used to measure the intensity of the hydroxyl stretching mode absorption band near 2.82-2.85 μ . A background correction was measured by drawing a base line between 2.65 and 3.85 μ .

The hydroxyl end group analysis by infrared and hence the equivalent weight determination was found to be independent of the P-BEP concentration in methyl ethyl ketone over the concentration range from 16 to 33 wt. % polymer in solution. The following equivalent weight data were obtained:

Apparent Equivalent
Weight by IR in MEK
(grams/mole of OH)

2270

2230

2230

2240

Average = 2240

(b) The Diborane Method

We also obtained equivalent weight data by the Diborane Method, an independent chemical method. This method had previously been applied successfully to OH-Telagen-S.

A series of measurements were carried out on P-BEP (9088-180A) which had been stripped to constant weight at a pressure of less than 10μ .

Equivalent Weight
by the Diborane Method
(grams/mole of OH)

1330

1280

1290

Average = 1300

This average equivalent weight of P-BEP indicates a considerably higher hydroxyl content than had been indicated by the IR equivalent weight data. The possibility of impurities which might respond to the Diborane reagent cannot be discounted.

Since the above two independent methods have given widely different results the need for a third independent equivalent weight method was indicated. For this reason an equivalent weight method based on the reaction of hydroxy-terminated prepolymers with toluenesulfonyl isocyanate was developed as described earlier in this report. The method was checked out with OH-Telagen-S and was subsequently extended to P-BEP.

(c) Reaction of P-BEP with
Toluenesulfonyl isocyanate

A series of five rate measurements of the reaction of P-BEP, 9088-180A with toluenesulfonyl isocyanate in dilute chloroform solution were made. The time dependence of the NCO absorbance at 4.47μ for two solutions is shown in Figures 34 and 35. A comparison of the P-BEP/TSNCO reaction curves with those for the Telagen-S/TSNCO system reveals some basic differences:

- the time dependence of the P-BEP/TSNCO reaction suggests the presence of two reactive species of different reactivity: (1) a reactive species having a reactivity similar to that of Telagen-S as indicated by the steep initial slope, and (2) a species of considerably lower reactivity as indicated by the curved portion of the reaction curve.
- over 95% of the P-BEP/TSNCO reaction at room temperature is complete after 2 to 3 hours.
- after 15 minutes the reaction is about 60% complete as compared to 100% for the corresponding Telagen-S/TSNCO reaction.

The calculated equivalent weight of P-BEP, 9088-180 A, based on five measurements is summarized below.

Equivalent Weight (grams/mole of OH)

1790
1640
1740
1805
1890

Average: 1770 grams/mole of OH

The equivalent weight of P-BEP, 9088-180A, (1770 grams/mole of OH) based on the P-BEP/TSNCO reaction lies between those values obtained by the infrared OH absorption method (2240) and the Diborane method (1300). We feel that the equivalent weight based on the reaction of P-BEP with toluenesulfonyl isocyanate represents the best value. In later determinations using purified P-BEP samples close agreement between the IR and the isocyanate method (TSNCO) was obtained.

5.3. Functionality Determination

The average functionality of P-BEP as calculated from equivalent weight data by the IR, Diborane and TSNCO method and average molecular weight measurements in benzene and dichloroethane [$\bar{M}_n = 3440$] by VPO is summarized below:

<u>Equivalent Weight Method</u>	<u>Equivalent Weight (grams/mole of OH)</u>	<u>Functionality</u>
IR	2240	1.54
Diborane	1300	2.65
TSNCO	1770	1.94

Figure 34. Reaction of P-BEP, 9088-180 A with toluenesulfonyl isocyanate in chloroform at room temperature. Change of isocyanate absorbance at 4.47μ with time. Concentration as indicated.

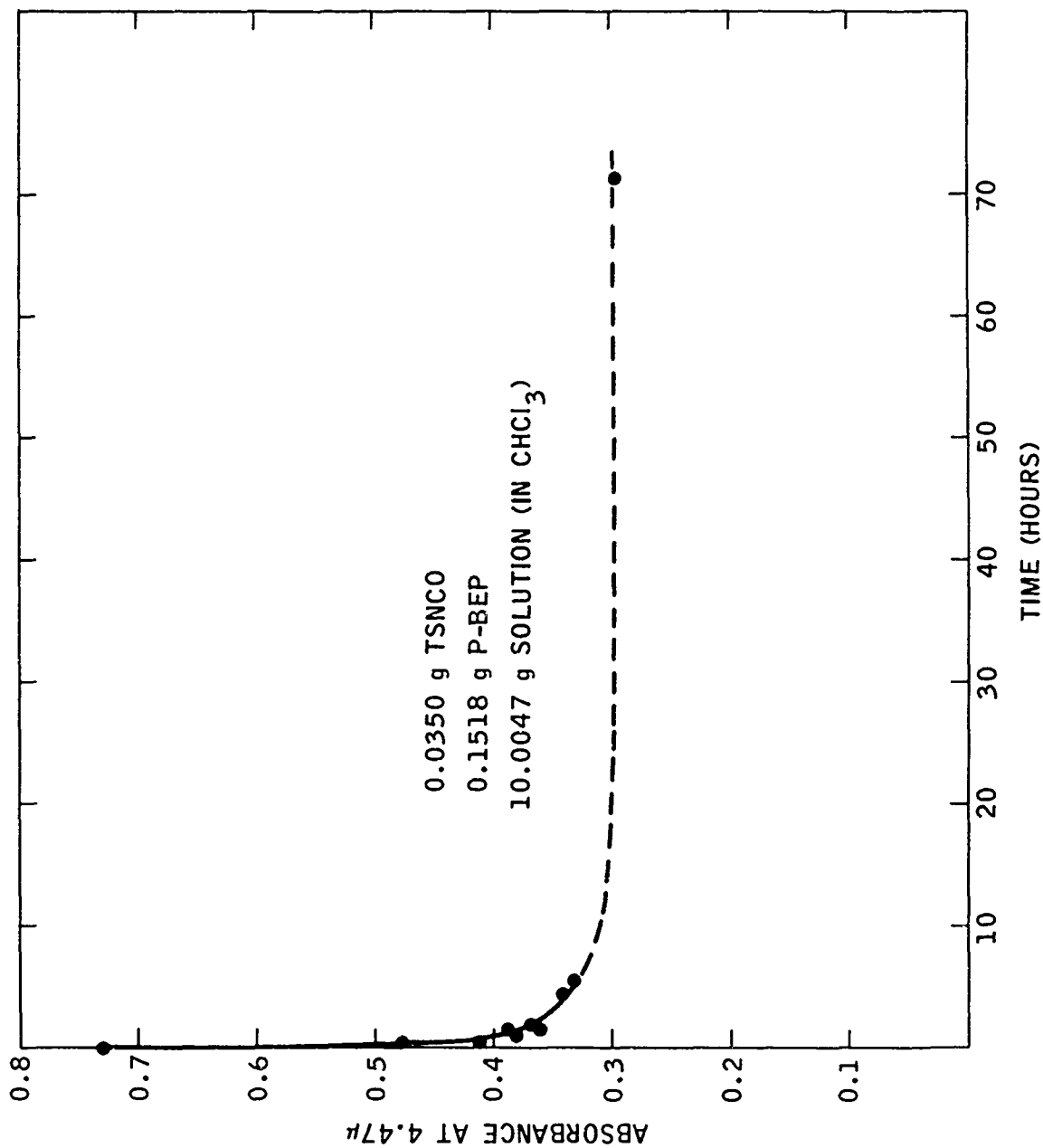
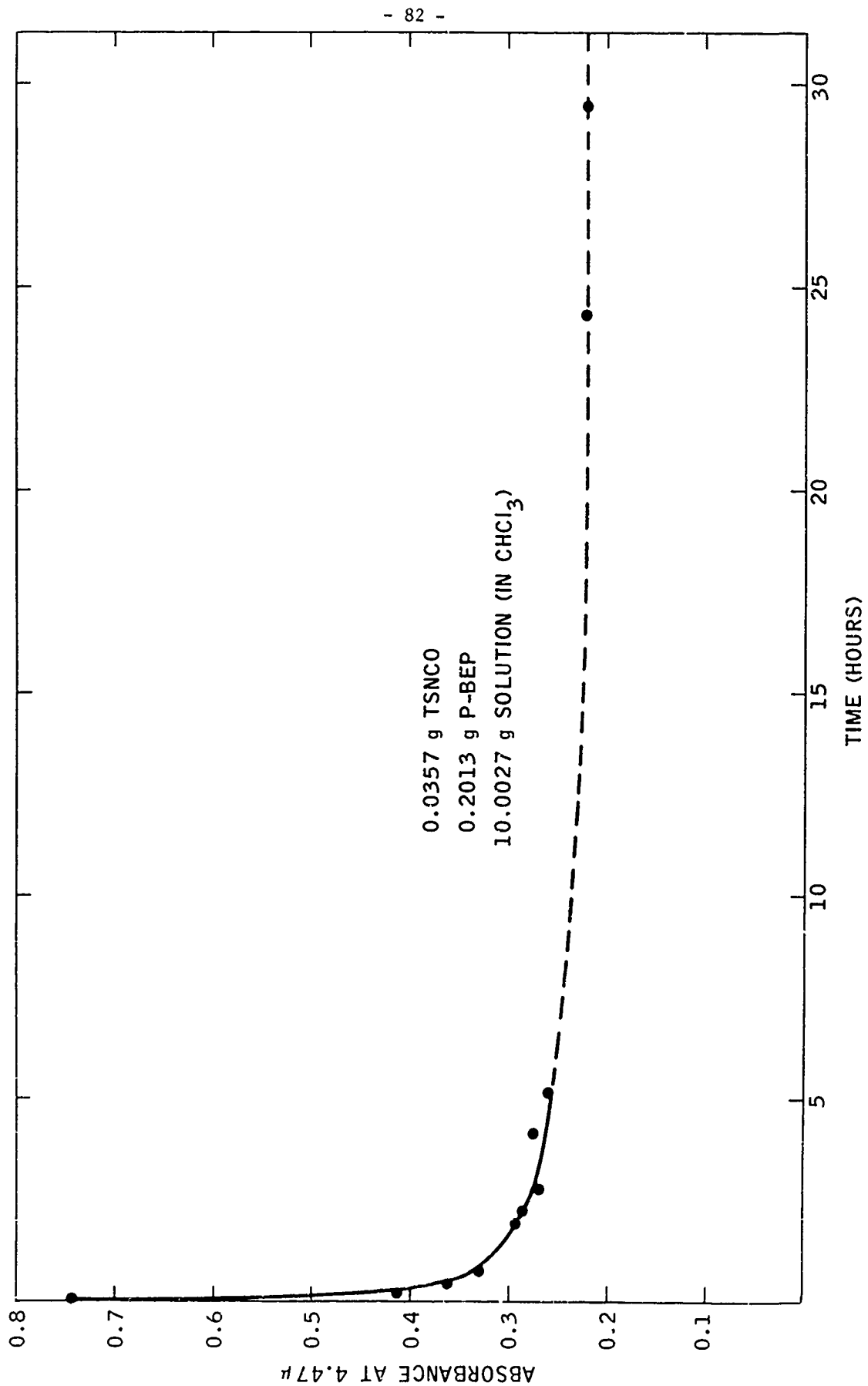


Figure 35. Reaction of P-BEP, 8088-180 A with toluenesulfonyl isocyanate in chloroform at room temperature.
Change of isocyanate absorbance at 4.47μ with time. Concentration as indicated.



We believe that the equivalent weight based on the reaction of P-BEP with TSNCO is the most reliable value.

5.4. Fractionation Studies

Fractionation studies based on adsorption of P-BEP on silica gel and subsequent selective desorption were carried out. The purpose of this study was to determine the functionality distribution of P-BEP, 9088-180A. The polymer was placed on the column in an approximate 50 wt. % solution in CHCl_3 . The gel/polymer ratio was 45/1. The polymer was eluted from the column by stepwise addition of CHCl_3 , CH_2Cl_2 and solvent mixtures of $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ and finally CH_3OH . The elution response is graphically summarized in Figure 36. Total polymer recovery was 96.6%. Molecular weight and equivalent weight data by IR were obtained on fractions I, II and III. The two remaining fractions were too small for meaningful molecular weight and equivalent weight analyses. Also, a small fraction (1.5 wt. %) eluted between fractions I and II was not analyzed. The concentration dependence of apparent molecular weight for fractions I, II and III is graphically shown in Figure 37.

All three fractions show very little concentration dependence of apparent molecular weight. Molecular weights $(\bar{M}_n)_0$ and IR equivalent weight data on the fractions are summarized below.

Fraction	Wt. %	$(\bar{M}_n)_0$	Equivalent Weight by IR in MEK grams/OH	Wavelength (μ) of OH Absorption Peaks of Neat P-BEP*	Remarks
I	34.0	5800 \pm 100	3250	2.78, (2.93), 3.0	--
II	34.3	2600 \pm 40	1840	2.78, (2.93)	Absorption at 4.42 μ
III	17.1	2580 \pm 25	1460	2.78, (2.93)	Absorption at 4.42 μ
IV	2.71	--	--	(3.0)	Absorption at 4.42 μ
V	6.96	--	--	(3.0)	Absorption at 4.42 μ

* Wavelength of major OH peak is placed in parenthesis ().

These data show that P-BEP 9088-180A contains a significant fraction of high molecular weight material of about 6000 number average molecular weight. Fractionation by molecular weight rather than functionality was obtained. Also there was definite evidence that decomposition had taken place. Fractions II through V showed absorption at 4.42 μ indicating the formation of nitrile groups. It is believed that the formation of nitrile functional groups interfered with the intended separation by OH-functionality.

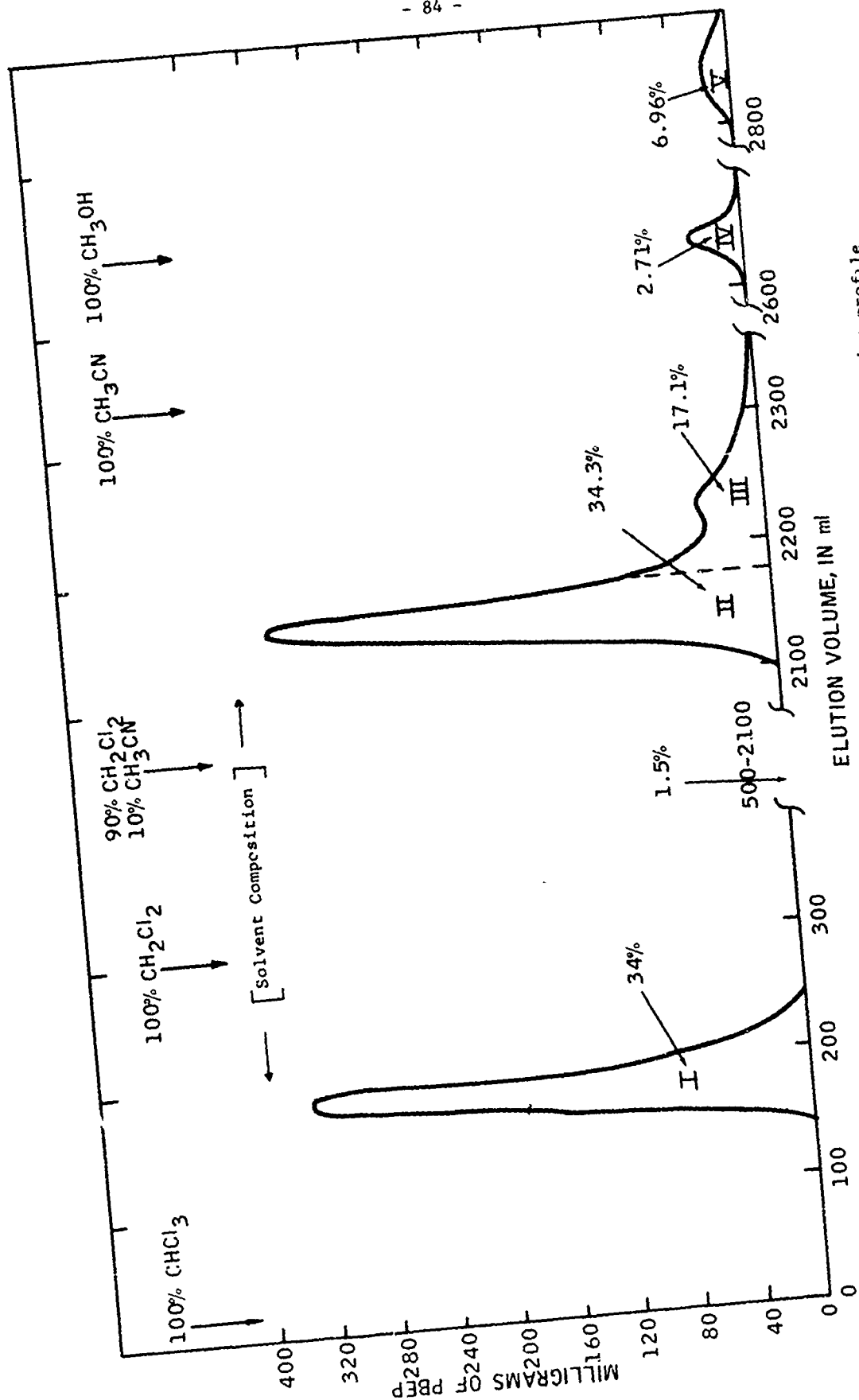


Figure 36. Fractionation of P-BEP, 9088-180A by elution from silica gel --- elution profile

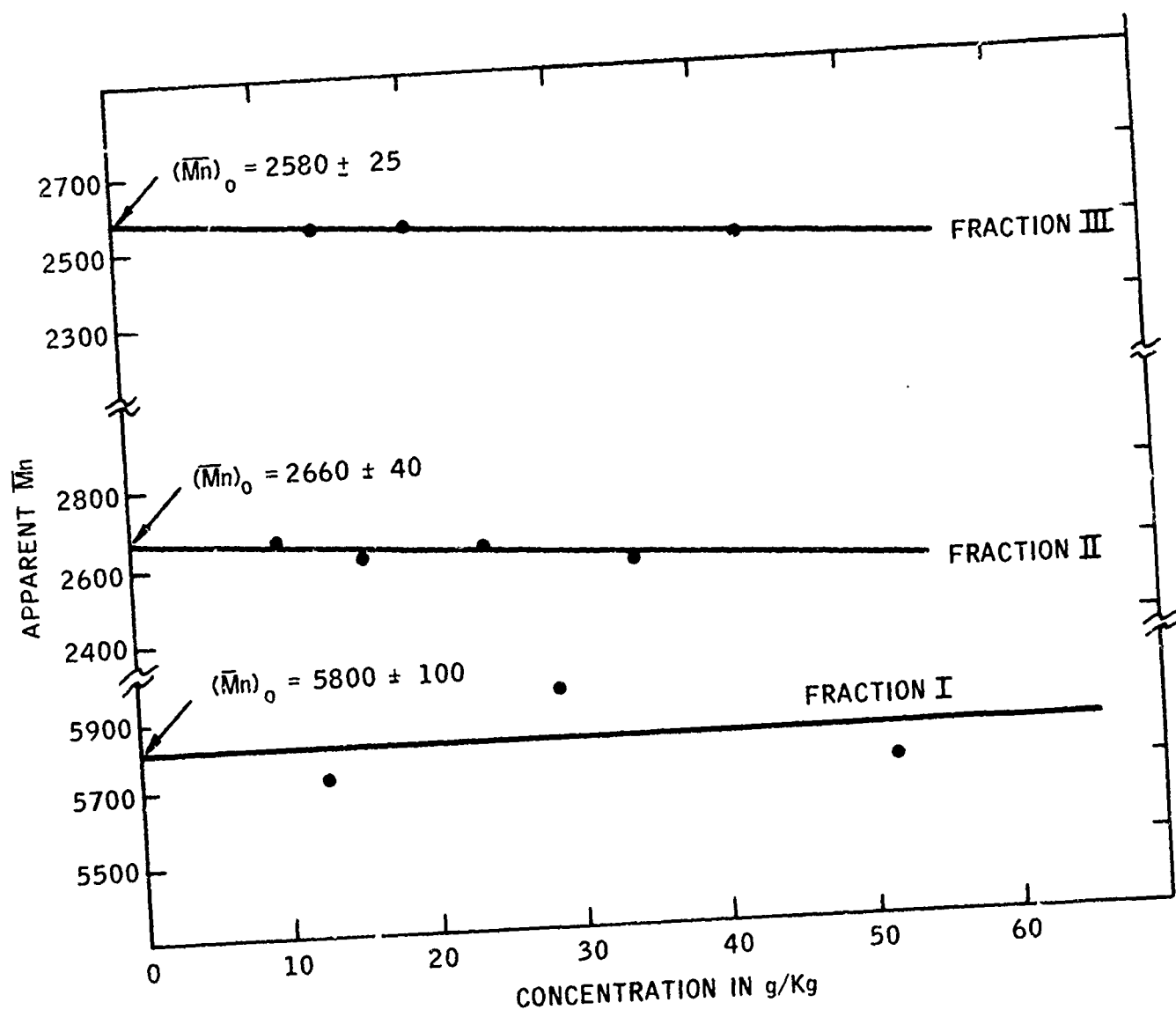


Figure 37. Dependence of apparent molecular weight (\bar{Mn}) on concentration for P-BEP fractions in 1,2-dichloroethane at 37°C

6. P-BEP, LOT 9542-60B

6.1. Equivalent Weight Measurements

A series of equivalent weight measurements of P-BEP 9542-60B have been made by reaction of the polymer with toluenesulfonyl isocyanate in dilute chloroform solution. The reaction of P-BEP 9542-60B with TSNCO shows the familiar profile which is characterized by two segments: a steep initial slope reflecting high reactivity, followed by a much lower reaction rate as reflected by the curved portion of the reaction profile. A typical reaction profile is shown in Figure 38. The results of four equivalent weight measurements are summarized below.

Equivalent Weight (grams/mole of OH)

2100
2120
2070
2100

Average: 2100 grams/mole of OH

The reproducibility of these measurements is excellent.

6.2. Functionality Determination

Molecular weight determinations by VPO in 1,2-dichloroethane gave a molecular weight of $(\overline{M}_n)_o = 3800$. This value is in excellent agreement with that reported by Shell ($\overline{M}_n = 3810$). Based on the equivalent weight of 2100 and a molecular weight of 3800 the calculated functionality is:

$$f = \frac{3800}{2100} = 1.81$$

6.3. Fractionation Studies on Different Adsorbents

Since previous fractionation studies of P-BEP on silica gel had indicated that decomposition was taking place on the column we carried out exploratory studies on a number of other adsorbents. P-BEP was found to be strongly adsorbed on 80-200 mesh acidic alumina, Brockman Activity I as well as neutral alumina. Methanol is required to desorb the polymer and polymer recovery was only about 25%. Fractionation on 80-200 mesh florisil, a synthetic magnesia, silica gel, gave higher recovery (60%) but offered no advantages over silica gel.

Fractionation on Activated Charcoal

Since silica gel and various alumina were found to be unsuitable adsorbents for P-BEP fractionation, we have extended our studies to activated charcoal. It was hoped that charcoal would have active sites which would preferentially adsorb the hydroxyl group of the prepolymer and hence permit selective desorption by functionality. A number of charcoals were considered. Many of the commercial charcoals were available only in powder

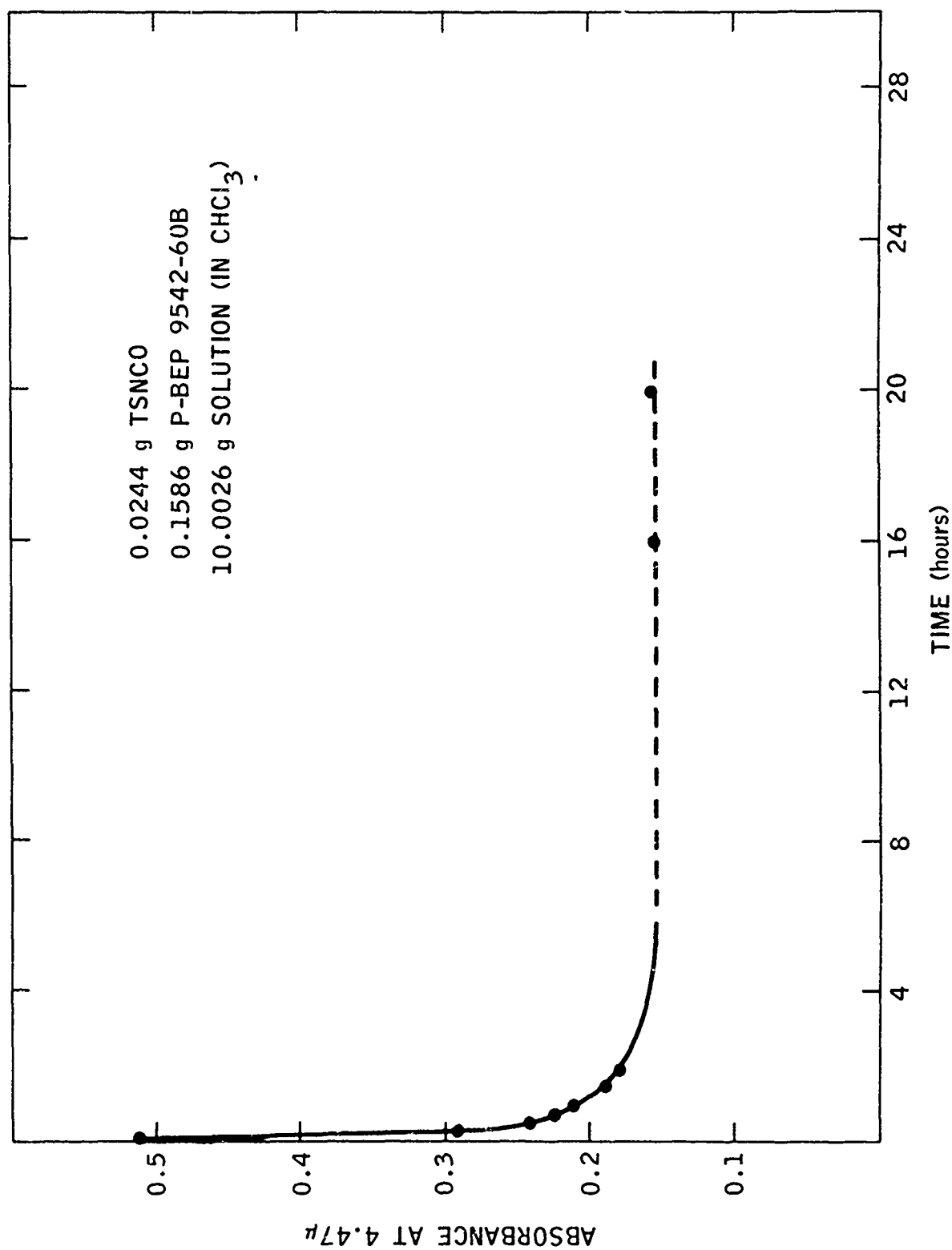


Figure 38. Reaction of P-BEP, 9542-60B with toluensulfonyl isocyanate in chloroform at room temperature. Change of isocyanate absorbance at 4.47 μ with time

form which could not be used. The particle size was too small and no solvent could be passed through the column even under pressure. Activated coconut charcoal of 20/40 mesh particle size was selected for the initial studies. Two different solvent systems were used. In one case the column was prepared in chloroform and the P-BEP eluted with chloroform and subsequently with acetonitrile. The polymer was essentially colorless. However, polymer recovery was only 67%. We have characterized the two major fractions which accounted for 25 and 27% respectively. The data summarized below suggest that there was a loss in functionality on the column.

<u>Wt % of Fraction</u>	<u>(Mn)₀</u>	<u>Equivalent Weight</u> (grams/mole of OH)	<u>Functionality</u>
25.0	3260	2780	1.17
27.0	2800	2160	1.30

In a second case, the column was prepared in 95/5 ethanol/water, a poor solvent for P-BEP. The following solvents were used in sequence: ethanol/water, ethanol, ethanol/acetonitrile, acetonitrile/methylene chloride and finally methylene chloride. Total recovery was only 28%. It is obvious that a significant portion of the polymer is irreversibly held on the charcoal and that the amount of polymer held on the column depends on the initial solvent used.

Fractionation of P-BEP on Ion Exchange Resins

We have explored the possibility of fractionating P-BEP by selective adsorption rather than ion exchange on the surface of ion exchange resins. The resins have a very large surface area and thus offer good possibilities for reversible adsorption. Two types of chromatographic grade Amberlite ion exchange resins of 200-400 mesh size were evaluated as potential adsorbents; CG-50-weakly acidic and CG-120-strongly acidic.

Fractionation on Amberlite CG-50 (200-400 mesh)

The column containing CG-50 resin was prepared in chloroform. The polymer was charged to the column in a 20% solution (in chloroform). The flow rate was controlled at 10 cc/hour. The resulting elution profile suggests that the P-BEP was only very weakly adsorbed. Total polymer recovery was 94%. The individual fractions were combined into three major fractions and characterized with respect to functionality. Infrared spectra of these fractions showed no evidence of decomposition.

Identification: 369-140

Amount of polymer fractionated: 0.946g

% recovery: 94%

<u>Fraction</u>	<u>% of Total</u>	<u>(Mn)₀</u>	<u>Equivalent Weight</u> (grams/mole of OH)	<u>Functionality</u>
I	28.0	2920	2200	1.33
II	49.8	3320	2540	1.31
III	16.2	5100	3230	1.58

The above data indicate some fractionation by molecular weight but no significant separation by functionality.

Fractionation on Amberlite
CG-120 (200-400 mesh)

Similar fractionation studies were carried out with Amberlite CG-120, a strongly acidic ion exchange resin. The elution profile was similar to that resulting from Amberlite CG-50. Total polymer recovery was 97.6%. Infrared spectra of the recovered fractions showed no evidence of decomposition. The individual fractions were combined into four major fractions and characterized with respect to functionality. The data indicate no separation by functionality or molecular weight.

Identification: 369-146

Polymer Charged to Column: 0.939g

% Recovery: 97.6%

<u>Fraction</u>	<u>% of Total</u>	<u>(Mn)_o</u>	<u>Equivalent Weight</u> (grams/mole OH)	<u>Functionality</u>
I	27.6	3500	2380	1.47
II	20.9	3840	2650	1.45
III	25.0	3400	2240	1.52
IV	24.1	3200	2150	1.49

Fractionation on MN-
Polyamide

Column chromatography of P-BEP, 9542-60B, on MN-polyamide powder, at an adsorbent to polymer ratio of 93/1 has been carried out. The bulk of the polymer (69%) is immediately eluted from the column in response to elution with chloroform. The remainder of the polymer is irreversibly held on the column. The eluted fraction (69%) is almost colorless but shows some haziness. Molecular weight measurements by VPO in chloroform at 37°C and equivalent weight measurements by reaction with toluenesulfonyl isocyanate have yielded the following results:

$(\overline{Mn})_o = 3200$

Equivalent Weight = 1550

Functionality = 2.06

Although this technique does not fractionate P-BEP by functionality the data suggest that a major fraction of improved functionality can be isolated. Further studies of this separation technique seem justified.

6.4. Molecular Weight Distribution and Dependence of Functionality on Molecular Weight

A 5 gram sample of P-BEP, 9542-60B, was fractionated by progressive addition of water to a P-BEP solution in ethanol at 25°C. A total of twelve fractions were isolated. Each fraction was equilibrated by redissolving it at 40°C, slowly cooling it to 25°C and letting the solution stand at 25°C for a period of 24 hours. To reduce the number of analyses, we have recombined the twelve fractions to yield 6 larger fractions. The fractions were stripped free of solvent with appropriate azeotropes at reduced pressures to remove traces of ethanol and water. The fractions were subsequently characterized with respect to number average molecular weight and equivalent weight. The purpose of this fractionation was to determine whether functionality varies with molecular weight.

Number average molecular weight measurements were carried out by VPO (Mechrolab 302) in chloroform at 37°C. The concentration dependence of the apparent molecular weight for the 6 fractions is shown in Figure 39. Fractions II through VI show essentially the same concentration dependence (same slope) over the concentration range 0.5 to 3.0 wt %. Only fraction I, the highest molecular weight fraction, showed a more pronounced concentration dependence. One general lesson can be learned from this observation: if a given polymeric material shows little or no concentration effect of molecular weight at one molecular weight level, it should not be concluded that the same concentration dependence will necessarily be observed at a higher molecular weight level.

The extrapolated molecular weights $(\bar{M}_n)_0$ were calculated by least square analysis of the data. Equivalent weights were determined by reaction with toluenesulfonyl isocyanate. A summary of the analyses are given in the table below. The analyses show that the molecular weight range of this P-BEP sample extends from below 700 to above 5000. Each of the terminal fractions (I and VI) undoubtedly has a molecular weight distribution so that the molecular weight range would go beyond these limits. This is particularly true for the high molecular weight fraction (fraction I) which accounts for 20% of the total polymer. The bulk of the polymer (60%) has a number average molecular weight above 3600. Figure 40 shows the integral molecular weight distribution curve of P-BEP, 9542-60B.

Summary of P-BEP, 9542-60B Fractionation

<u>Fraction</u>	<u>Wt %</u>	<u>$(\bar{M}_n)_0$</u>	<u>Equivalent Weight (Grams/Mole of OH)</u>	<u>Functionality</u>
I	20.2	5080	3200	1.59
II	17.7	4000	2390	1.67
III	22.3	3590	2500	1.44
IV	17.6	2770	1870	1.48
V	12.5	1500	1510	0.99
VI	<u>5.3</u>	680	790	0.86
	95.6%			

The functionality of these fractions is of particular interest. About 78 wt % of the polymer (fractions I through IV) has a functionality of 1.44 to 1.67. For these fractions, which cover the molecular weight range from 2800 to 5100, there is no significant dependence of functionality on molecular weight. In the low molecular weight range (1500 and below), however, there is a significant decrease in functionality, the functionality dropping below 1.0. The dependence of functionality on molecular weight is graphically represented in Figure 41.

Since this fractionation technique does not separate polymer by functionality, each fraction is likely to have a functionality distribution. The values listed in the table only reflect the average functionality of each fraction and it is impossible to speculate on the functionality distribution within each fraction.

The fact that the overall functionality of the polymer is greater than each of the fractions suggests that some degradation has taken place during the fractionation.

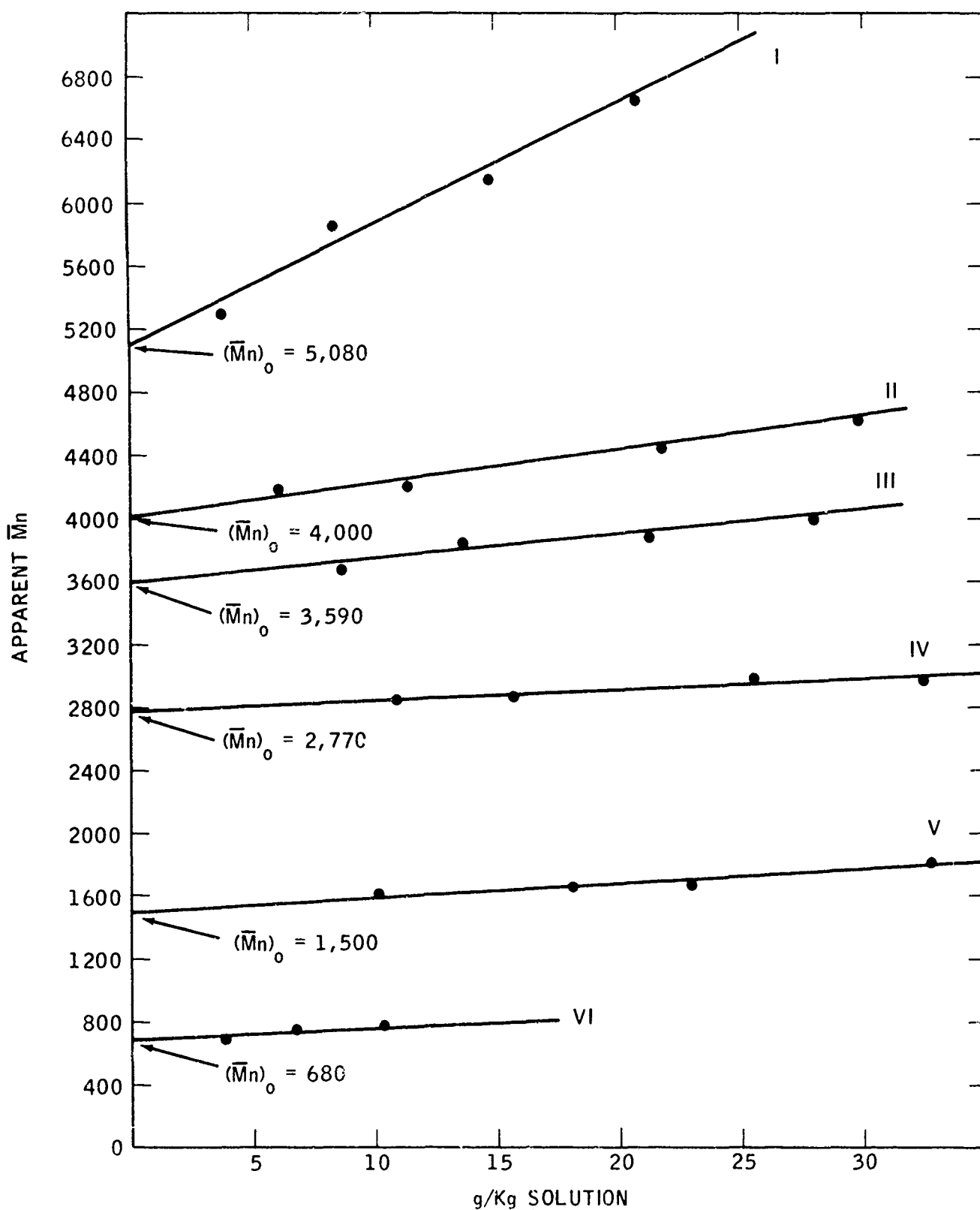


Figure 39. Concentration dependence of molecular weight for P-BEP, 9542-60B, fractions by VPO in chloroform at 37°C

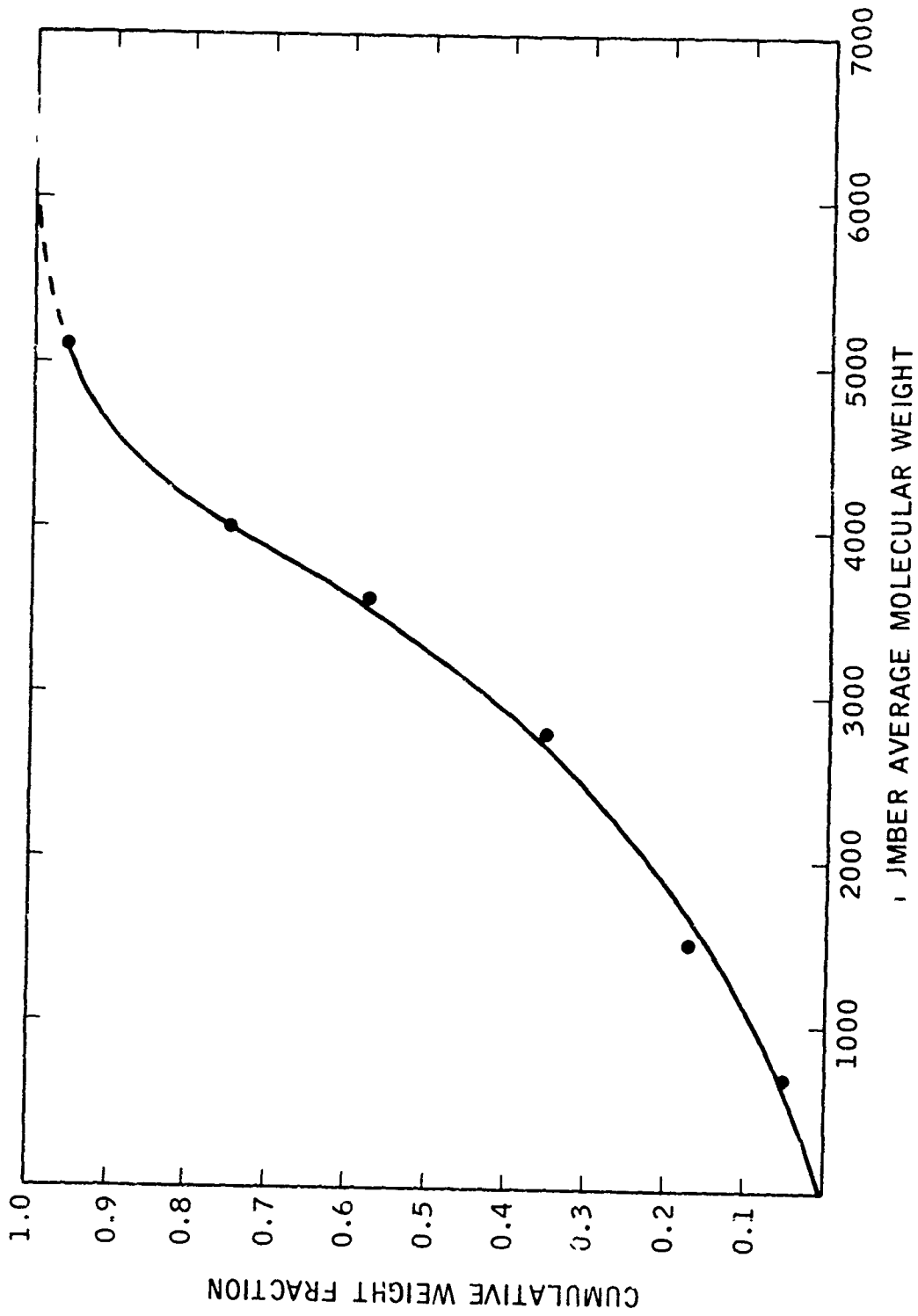


Figure 40. Integral molecular weight distribution curve of P-BEP, 9542-60B.

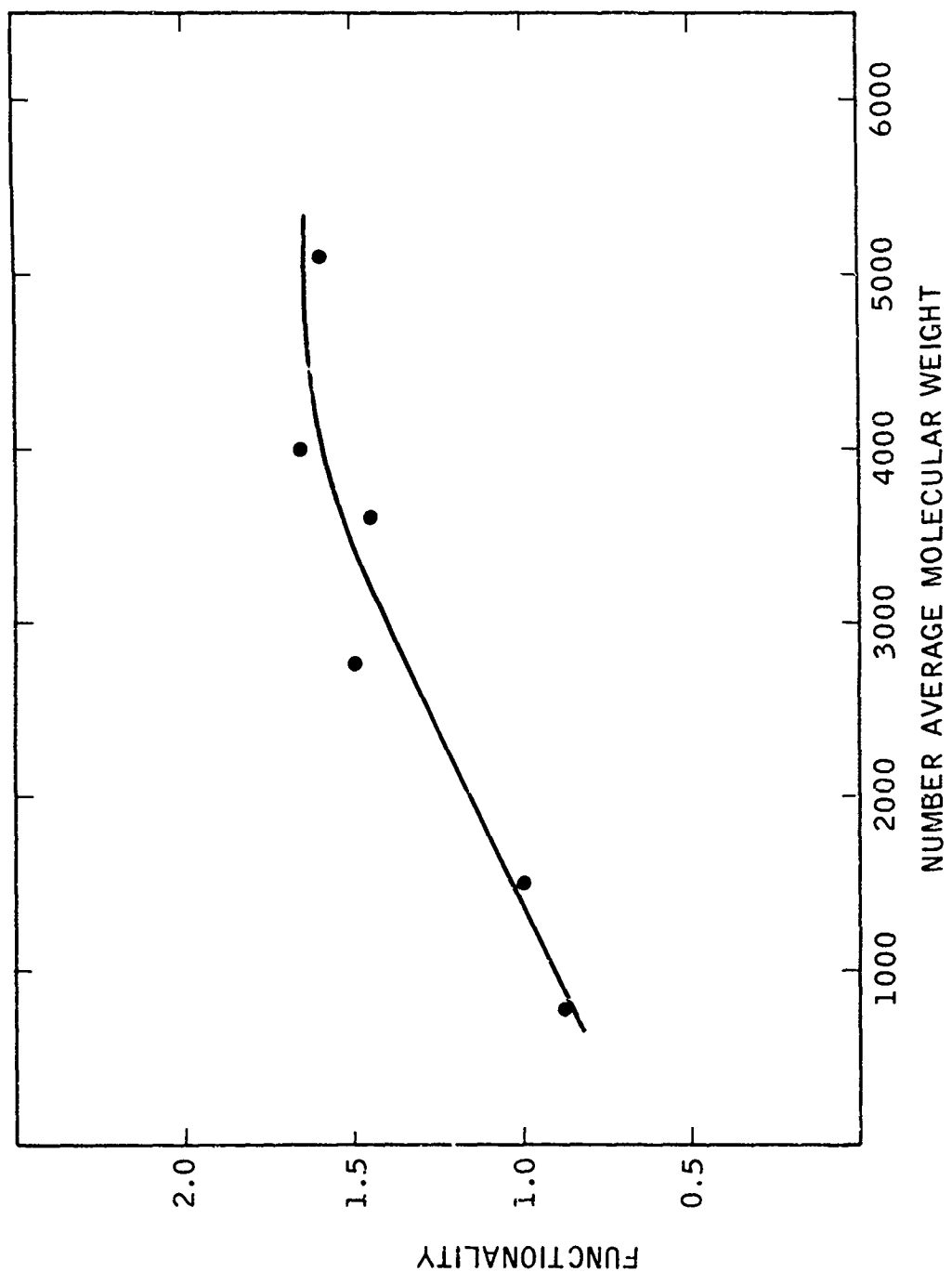


Figure 41. Dependence of functionality on molecular weight for P-BEP, 9542-60B.

7. P-BEP, LOT 10316-115

A 5.5 lb sample of P-BEP, 10316-115, was recently received from the Shell Development Company for curing studies under Contract FO4611-68-C-0045. We have characterized this sample with respect to equivalent weight and molecular weight.

7.1. Equivalent Weight Determinations

Equivalent weight measurements were made by reacting the polymer in solution with p-toluenesulfonyl isocyanate (TSNCO) at room temperature. The results are summarized below:

Equivalent Weight

(Grams/mole of OH)

1950
1955
2030

average: 1980 g/mole of OH

Shell has reported the following equivalent weight determinations on this polymer based on two different methods.

Hydroxy Content by IR

0.049 eg/100 g
= 2040 g/mole of OH

"NCO Equivalent"

0.062 eg/100 g
= 1610 g/mole of OH

The equivalent weight measurements by reaction with TSNCO are in good agreement with Shell's hydroxyl determination by infrared. The "NCO Equivalent" which is based on the amount of tolylene diisocyanate required to give maximum viscosity differs considerably from these values.

7.2. Molecular Weight Measurements

The polymer was stripped as a thin film under vacuum at 40°C before molecular weight measurements were carried out by VPO in chloroform at 37°C. The apparent molecular weight shows a slight concentration dependence as shown in Figure 42. Least square analysis of the data gave a $(\bar{M}_n)_o = 3960$. Shell has reported a slightly lower molecular weight by VPO in ethylene dichloride ($\bar{M}_n = 3630$).

7.3. Functionality

The calculated functionality based on the molecular weight of 3960 and the equivalent weight of 1980 is $f = 2.0$. This P-BEP sample has a significantly higher functionality than previous samples received from Shell which had functionalities of 1.6-1.8.

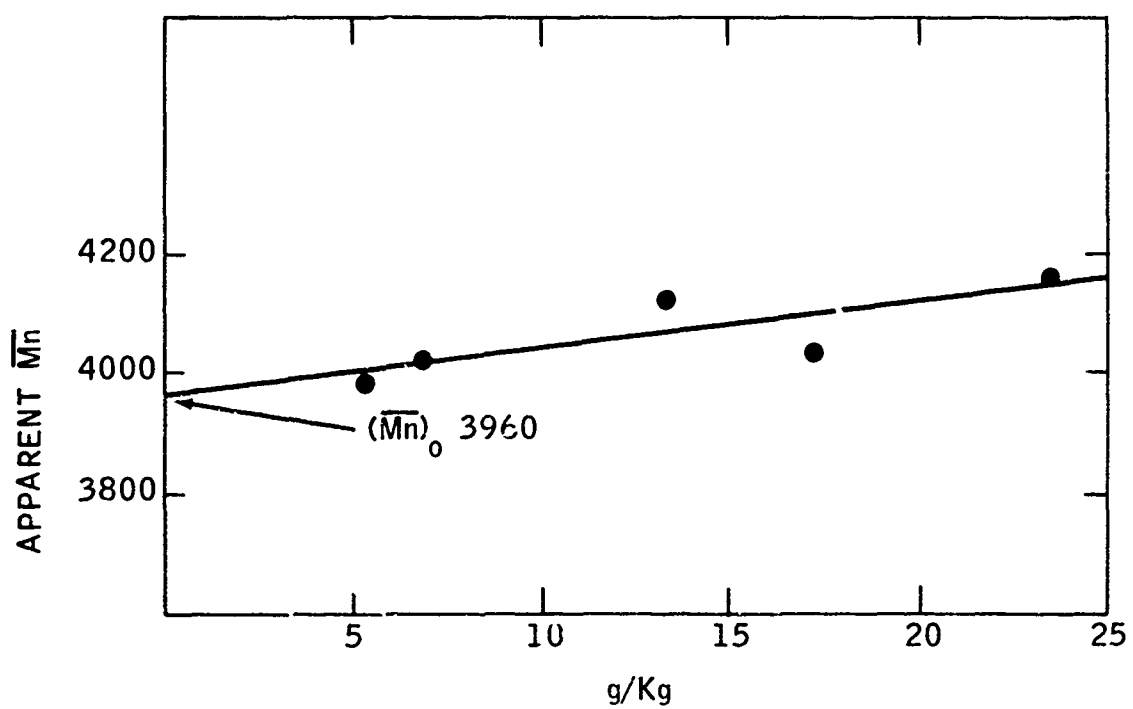


Figure 42. Concentration dependence of molecular weight for P-BEP, 10316-115, in chloroform at 37°C.

8. CNR-NITROSO TERPOLYMER

A sample of CNR-nitroso prepolymer, lot A001-4D, from the Reaction Motors Division of Thiokol Chemical Corporation was characterized with respect to functionality and functionality distribution. This represented the first sample of a fluorocarbon prepolymer received for characterization under this program.

This prepolymer which contains carboxy functional groups along the chain, is prepared by terpolymerization of trifluoronitrosomethane (CF_2NO), tetrafluoroethylene ($\text{CF}_2=\text{CF}_2$) and a nitrosoperfluoro acid. Because of solubility limitations and the highly acidic character of the perfluoro acid groups, the techniques previously developed for the determination of functionality and functionality distribution were not directly applicable. Modified techniques were therefore needed, particularly with respect to the determination of functionality distribution.

8.1. Molecular Weight Measurements by VPO in Freon-215 at 37°C

The CNR-nitroso terpolymer is soluble only in a limited number of fluorinated solvents. 3M's FC-43 and FC-75 have been reported to be good solvents for this polymer. Since these solvents are solvent mixtures they are not applicable, however, for molecular weight measurements by VPO. Thiokol has used hexafluorobenzene for Mn measurements. This solvent is, however, extremely expensive. We have found that Freon-215, trichloropentafluoropropane, is a very good solvent for this polymer. Freon-215 is available from Dupont.

Molecular weight measurements were therefore carried out with Freon-215 at 37°C using the recently purchased Hitachi Perkin-Elmer Molecular Weight Apparatus. Figure 43 shows the concentration dependence of molecular weight for CNR-nitroso prepolymer, lot A001-4D. The slope of the line indicates only moderate dependence of molecular weight on concentration. Least square analysis of the data results in an extrapolated molecular weight of $(M_n)_0 = 4950$. A significant amount of volatiles (1.7%) was found in the polymer. Our molecular weight determinations were made on the completely stripped polymer.

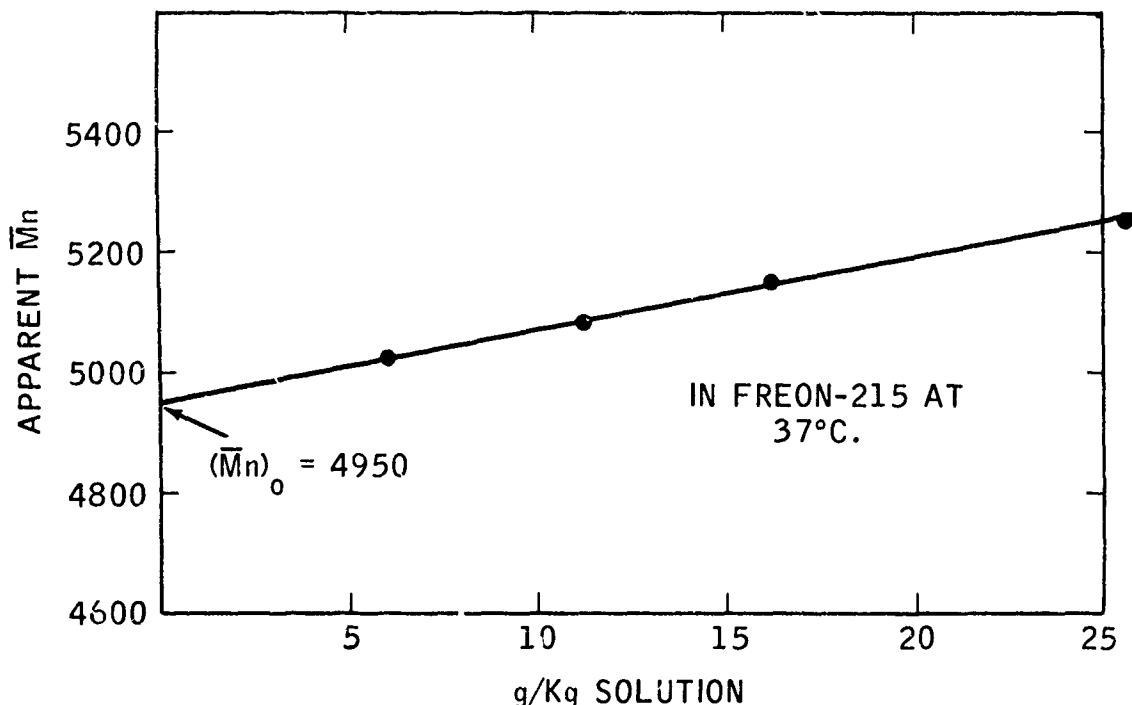


Figure 43. Concentration dependence of molecular weight for CNR-Nitroso Rubber Lot A001-4D in Freon-215 (trichloropentafluoropropane) at 37°C

8.2. Equivalent Weight Determination by Base Titration and Infrared Absorption Measurements

The COOH-equivalent weight of nitroso-prepolymer, lot A001-4D, was determined by: (1) base titration of a Freon-215 solution of the polymer with 0.1 N tetrabutyl ammonium hydroxide in methanol, and by (2) infrared absorption measurements of the polymer in solution. The latter method is based on measuring the intensity of the carbonyl absorption band in the infrared (5.72μ). The method is nondestructive and requires only small polymer samples. It is therefore ideally suited for the characterization of small fractions of CNR-nitroso terpolymer for the purpose of determining the functionality distribution. In the case of the infrared absorption method the problem is essentially one of finding a solvent or solvent mixture which will give a linear response of the intensity of the carbonyl absorption band with COOH concentration. A calibration is therefore needed which relates the intensity of the carbonyl absorption band to the molar concentration of the calibrant.

In selecting a suitable calibrant two approaches are possible: (1) Simulate the functional group of the prepolymer by using a perfluoro acid as the calibrant; we have chosen pentafluoropropionic acid as the calibrant. (2) An alternate method is to use the nitroso-prepolymer whose equivalent weight has been accurately determined by base titration, as the calibrant.

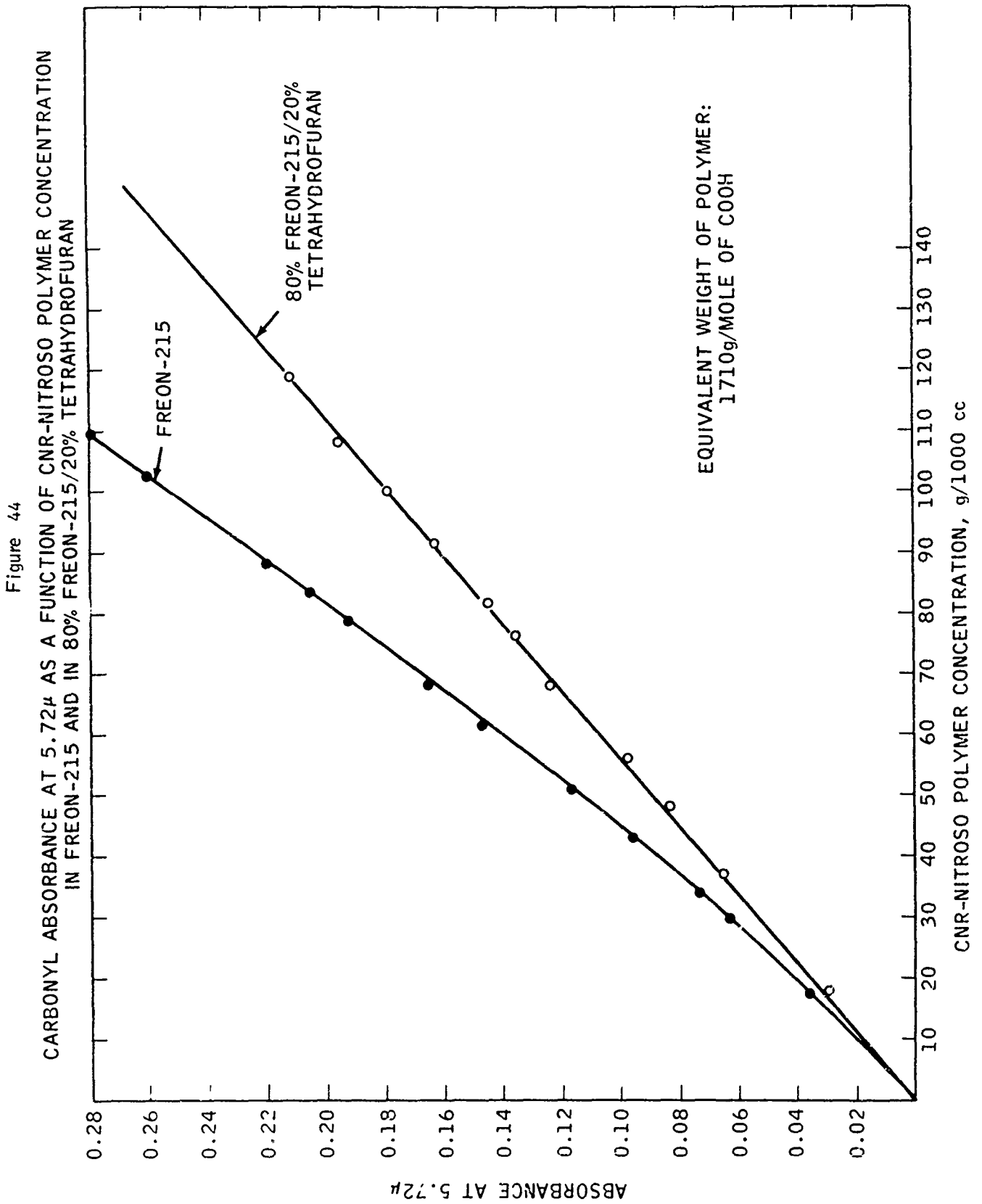
Figure 44 shows the correlation of the intensity of the carbonyl absorbance at 5.72μ as a function of CNR-nitroso polymer concentration in both Freon-215 and in a solvent mixture of 80% Freon-215/20% Tetrahydrofuran. Freon-215 gives higher sensitivity but exhibits a slightly nonlinear relationship. The 80% Freon-215/20% Tetrahydrofuran solvent mixture gives a linear response and was therefore used for equivalent weight measurements.

Figure 45 shows the correlation of the intensity of the carbonyl absorbance at 5.72μ as a function of molar concentration of pentafluoropropionic acid.

The results of the equivalent weight determination by base titration and infrared absorption measurements (using pentafluoropropionic acid as the calibrant) are summarized below:

COOH-Equivalent Weight (Grams/Mole COOH)	
<u>Titration with 0.1 N Tetrabutyl Ammonium Hydroxide</u>	<u>Infrared Absorption Measurements at 5.72μ (Pentafluoropropionic acid calibrant)</u>
1690	
1700	1580
1740	1620
<u>1700</u>	<u>1610</u>
Avg: 1710	Avg: 1600

The average of the equivalent weight measurements by the infrared absorption method (pentafluoropropionic acid calibrant) differs by about 6% from the average value obtained by the base titration method. Although the agreement is fair it seems advisable to use the nitroso-prepolymer of known equivalent weight as the calibrant (in place of pentafluoropropionic acid) for the infrared absorption technique when characterizing small nitroso-prepolymer fractions. In the latter case, there would be of course complete agreement between the base titration and the infrared absorption method.



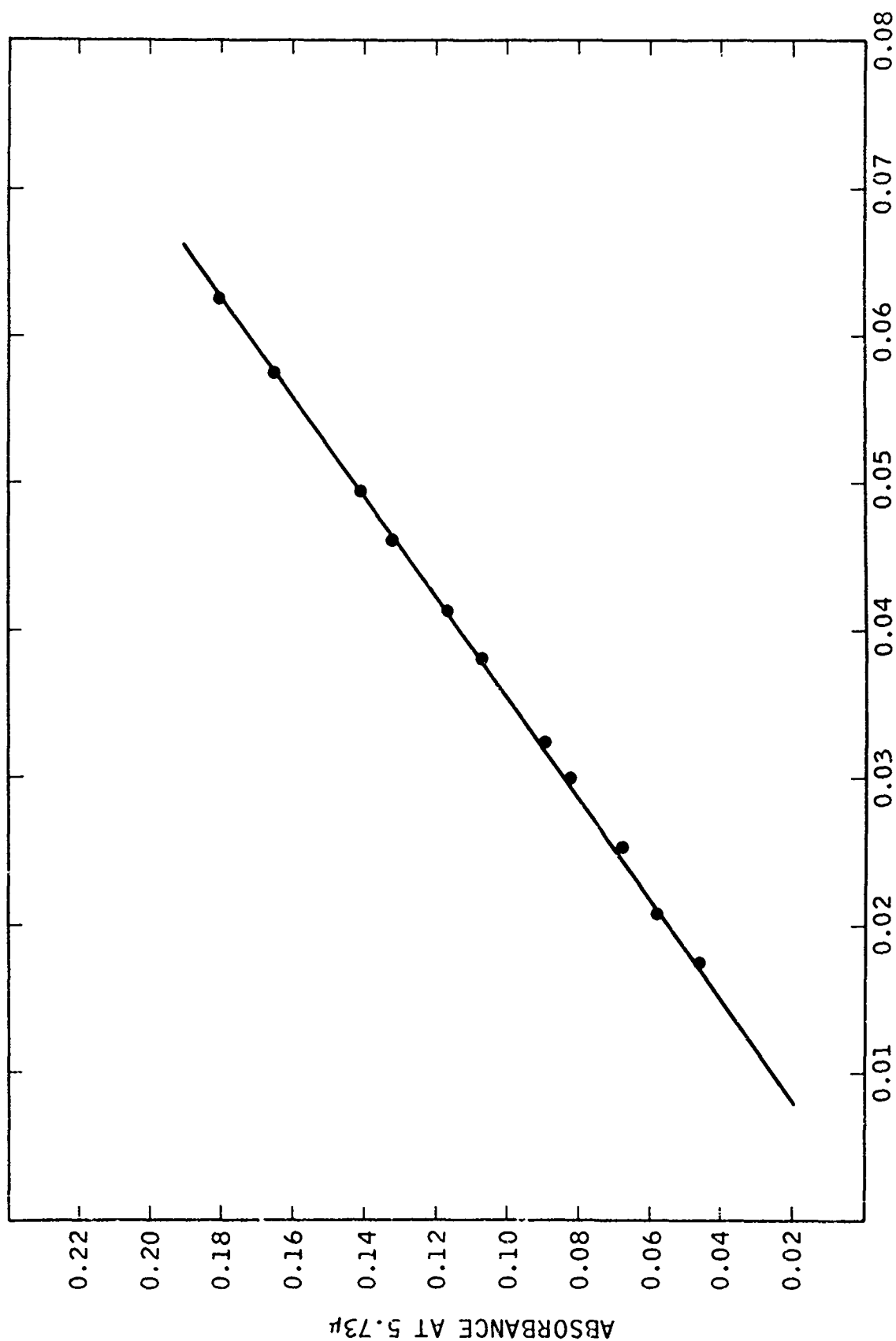


Figure 45. COOH-calibration: pentafluoropropionic acid in 80% Freon-215/20% tetrahydrofuran, Beckman IR-8, using matched liquid absorption cells of about 0.10 mm thickness.

8.3. Functionality of Nitroso-Terpolymer, A001-4D

Based on the number average molecular weight of $(M_n)_o = 4950$ and the equivalent weight of 1710 by base titration the calculated functionality is:

$$f = \frac{4950}{1710} = 2.9$$

This value suggests that the bulk of the material has a functionality of about 3.0. The polymer obviously has a functionality distribution extending from nonfunctional polymer to polymer components having functionality greater than 3.

8.4. Functionality Distribution Measurements of CNR-Nitroso Prepolymer, Lot A001-4D

Difficulties were initially encountered when attempting to adapt the functionality distribution method for the hydrogenated COOH-terminated polybutadienes and polyisobutylenes to the CNR-nitroso prepolymer.

There are two main differences between the CNR-nitroso and previously characterized COOH-terminated prepolymers:

- (1) the CNR-nitroso prepolymer is soluble only in a limited number of fluorinated solvents.
- (2) the CNR-prepolymer does not have terminal COOH-functional groups but rather a distribution of COOH-groups along the chain. For this reason we expect to find a distribution of functionalities extending from 0 to above 3.

Three different adsorbents (silica gel, acidic alumina and florisil) were explored which all gave quantitative separation of the nonfunctional prepolymer components which account for 9.9% of the polymer. In addition to getting poor polymer recovery, however, degradation was taking place on the column as evidenced by infrared absorption measurements. In order to prevent polymer degradation on the column, we passivated the silica gel column by passing a 98% Freon-215/2% trifluoroacetic acid mixture through the column before placing the polymer on the adsorbent. As a result polymer fractions eluted from the column showed no evidence of degradation. Because of the decreased activity of the silica gel the nonfunctional polymer fraction is eluted together with the first functional fraction. The nonfunctional polymer component had previously been isolated and reproducibly accounted for 9.9 wt% of the total polymer. The first fraction (I) of fractionation 369-156 which accounts for 20.6 wt.% and has a functionality of 0.51 therefore contains 48% nonfunctional (9.9% of total) and 52% monofunctional prepolymer (10.7 wt% of total).

Because of the difficulty of recovering the polymer, the fractionation was carried out at a very low gel/polymer ratio (17/1). Even at this ratio total polymer recovery was only 81 wt%. The remaining 19 wt% was irreversibly adsorbed on the column and could not be recovered. Fractionation parameters and analyses of the polymer fractions are summarized below.

Identification:	369-156
Silica gel/polymer ratio:	17/1
Polymer charged to column:	1.475 g
Total polymer recovery:	81%

<u>Fraction</u>	<u>Wt% of Total</u>	<u>(Mn)_o</u>	<u>Equivalent Weight</u> <u>(grams/mole COOH)</u>	<u>Functionality</u>
I	20.6*	3300	6430	0.51
II	20.2	4350	2190	1.99
III	17.5	6500	1760	3.69
IV	20.7	7500	1460	5.14
V	2.0	--	--	--
	81.0%			

* Contains a 9.9% nonfunctional fraction

The elution profile shown in Figure 46 shows three major peaks and a series of minor peaks. It is quite apparent from the profile that it becomes progressively more difficult to desorb the polymer of high functionality.

Figure 47 shows the concentration dependence of molecular weight for fractions I through IV as well as the total polymer. The two higher molecular weight fractions show a somewhat greater concentration dependence than the lower molecular weight fractions. This trend has been observed for other polymers as well.

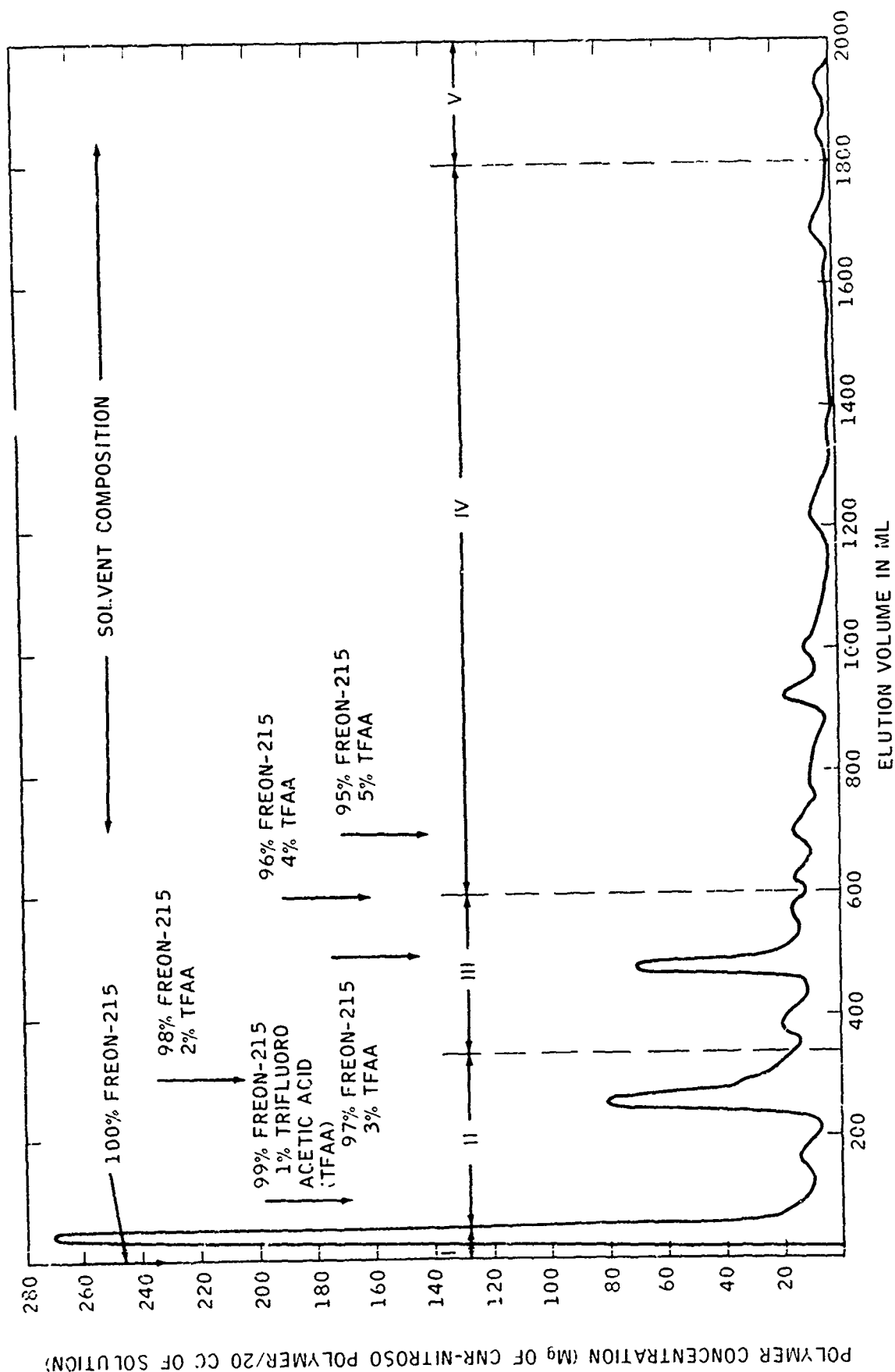
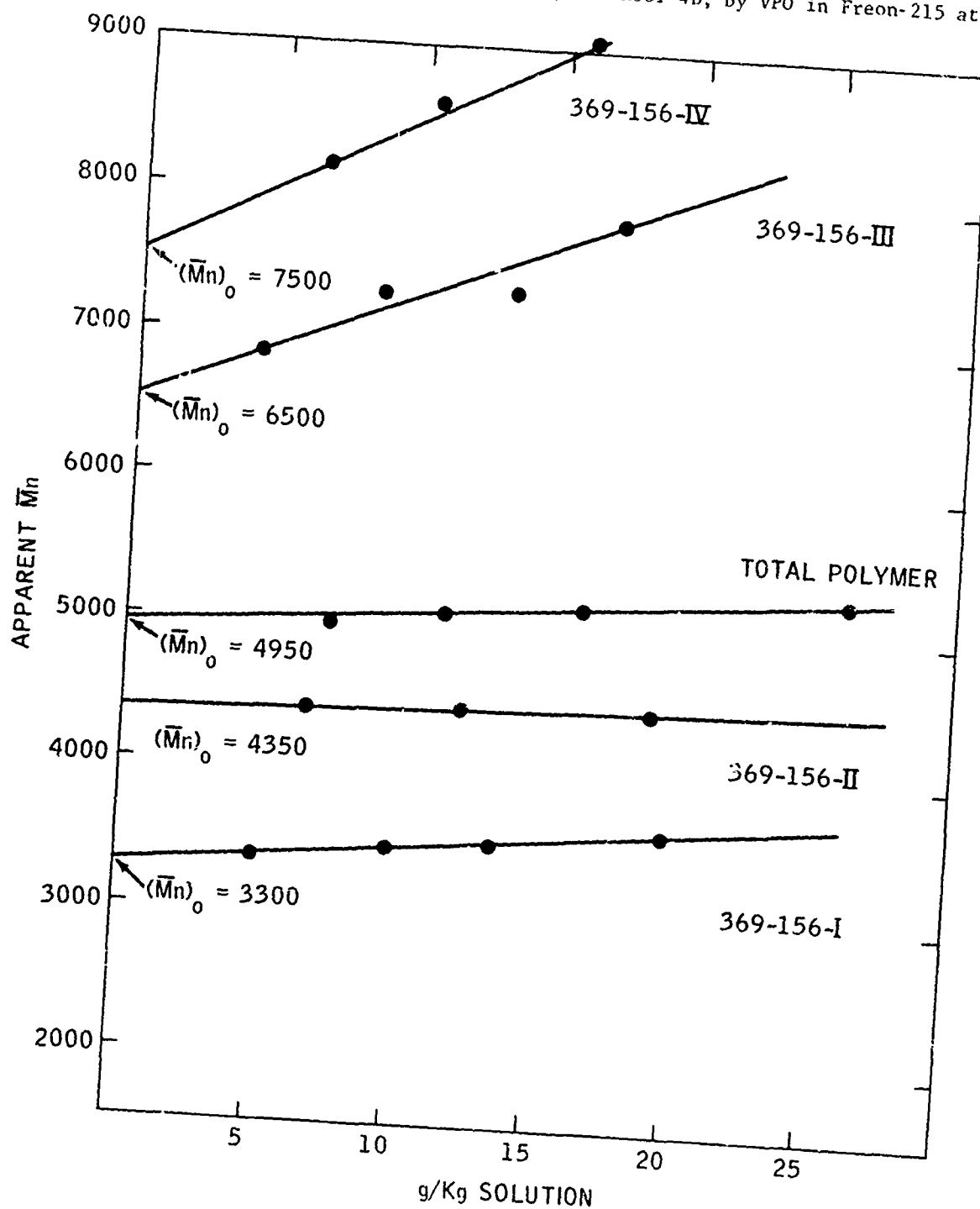


Figure 46 Fractionation of CNR-nitroso terpolymer, lot A001-4D, by stepwise elution from silica gel
elution profile of fractionation 369-156, silica gel/polymer = 17/1

Analysis of fractions I through IV allows the following conclusions:

- The polymer was eluted from the column in order of increasing functionality.
- Functionality increases with increase in molecular weight.
- The polymer has a functionality distribution extending from nonfunctional polymer to components having functionalities greater than 5.0.
- Fraction I which accounts for 20.6 wt% of the total polymer has an average functionality of 0.51. Previous fractionation studies had shown that the total polymer contains 9.9 wt% of nonfunctional polymer which is non-adsorbed on silica gel and therefore is eluted first from the column. Fraction I is therefore a mixture of nonfunctional (9.9%) and mono-functional (10.7%) polymer based on its overall functionality of 0.51,
- Fraction II which accounts for 20 wt% of the total polymer is difunctional.
- Fraction III comprises 17 to 18% of the polymer and contains tri- and tetrafunctional polymers.
- Fraction IV is essentially penta-functional. It accounts for about 21% of the polymer.
- Projection of these data to the remaining 20% which could not be desorbed suggest that the remainder has a functionality in excess of 5.0.

Figure 47. Concentration dependence of molecular weight for polymer fractions of CNR-nitroso-terpolymer, lot A001-4D, by VPO in Freon-215 at 37°C.



Infrared spectra of the whole polymer, the nonfunctional prepolymer fraction previously isolated, and fractions I through IV of fractionation 369-156 are shown in Appendix B-8.

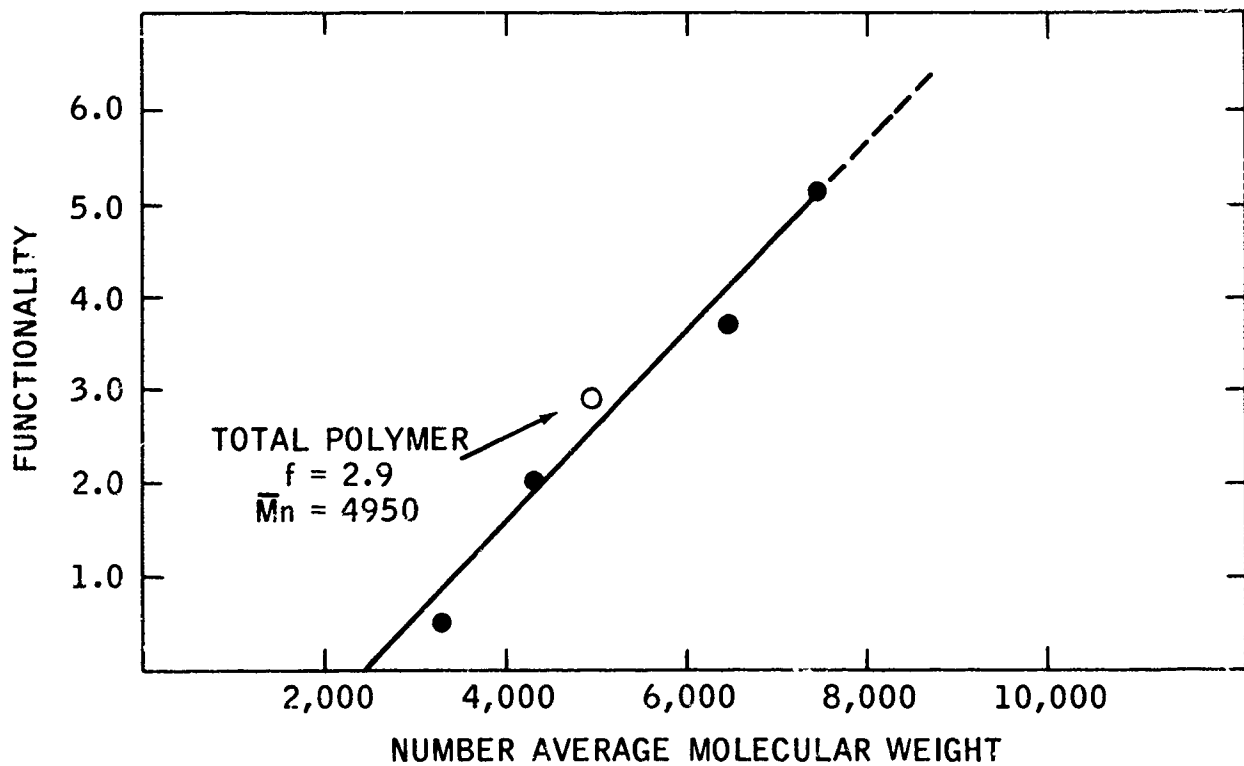
In summary the approximate functionality distribution of CNR-nitroso prepolymer lot A001-4D is:

- 10% nonfunctional
- 10-11% monofunctional
- 20% difunctional
- 17-18% tri- and tetrafunctional
- 20-21% pentafunctional
- 20% in excess of a functionality of 5.0

These data are consistent with the overall functionality of the total polymer which had been determined to be 2.9.

The strong dependence of functionality on molecular weight is illustrated in Figure 48. This dependence is not surprising since the number of nitroso perfluoro acid monomer units incorporated into the polymer chain should increase with increase in chain length.

Figure 48. Correlation of functionality with molecular weight for CNR-nitroso terpolymer, lot A001-4D



9. 3M'S HYDROXY-FUNCTIONAL PERFLUOROALKYLENE
OXIDE PREPOLYMER

We received a small sample of 3M's hydroxy-functional perfluoro-alkylene oxide prepolymer for characterization under this program. Functionally-terminated perfluoroalkylene oxide prepolymers are of interest as propellant binders because of their high density and thermal stability.

9.1. Molecular Weight Measurements

Molecular weight measurements were carried out by VPO in ethyl acetate at 37°C using the Hitachi Perkin-Elmer Molecular Weight Apparatus. The concentration dependence of molecular weight is shown in Figure 49. The extrapolated molecular weight, $(\bar{M}_n)_0$, is 1240.

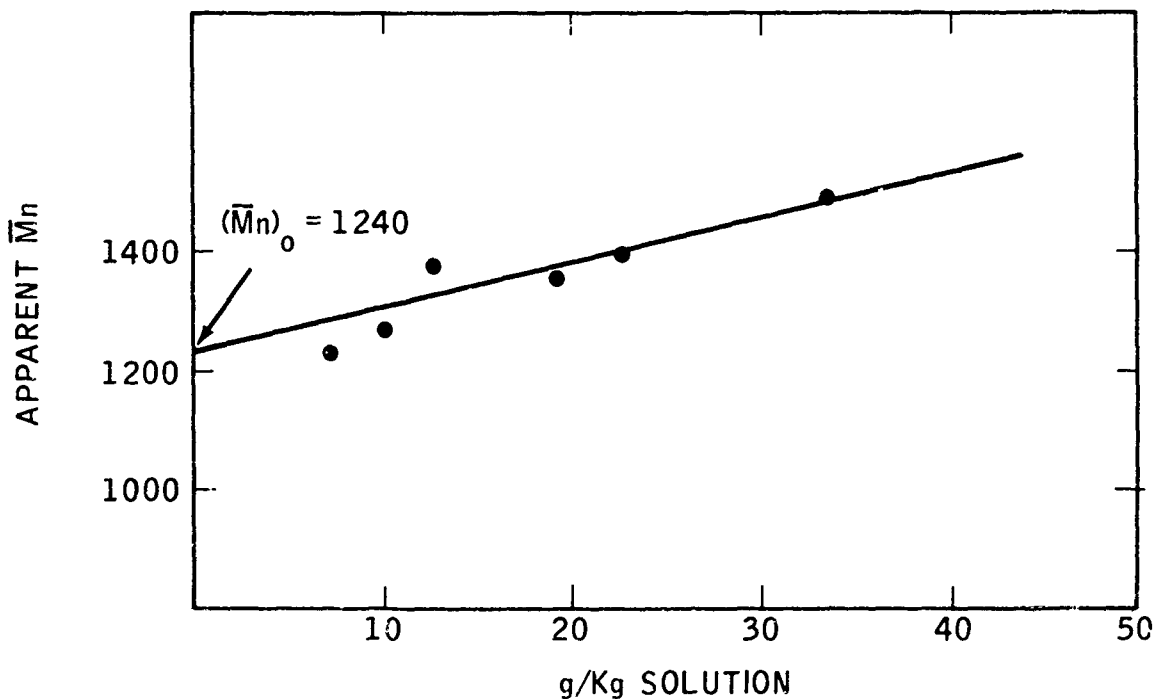


Figure 49. Concentration dependence of molecular weight for 3M's hydroxy-functional perfluoroalkylene oxide prepolymer in ethyl acetate at 37°C using the Hitachi Perkin-Elmer molecular weight apparatus.

9.2. Equivalent Weight Determinations

Studies have been carried out to adapt the equivalent weight determination based on the reaction of hydroxy-functional groups of the polymer with toluenesulfonyl isocyanate. The preferred solvent, chloroform, for this reaction cannot be used in this case because the 3M polymer is not soluble in chloroform.

We have therefore investigated ethyl acetate as an acceptable solvent for this reaction. The ethyl acetate was first pretreated with a small amount of toluenesulfonyl isocyanate (TSNCO) to react with residual water. When there was no further consumption of the isocyanate the solvent was assumed to be free of water. As usual all studies with the toluenesulfonyl isocyanate were carried out under dry box conditions.

The reaction profile of the 3M polymer with TSNCO in ethyl acetate indicated that a side reaction was taking place. After the initial reaction the remaining isocyanate was slowly consumed until it was reduced to zero. We have therefore attempted to measure the equivalent weight by two other methods:

- by reacting the polymer with a conventional isocyanate, phenyl isocyanate, in the presence of a catalyst and
- by measuring the intensity of the hydroxyl absorption band of the polymer in ethyl acetate and relating the absorption intensity to a calibration of butanol in the same solvent.

Reaction of Polymer with Phenyl Isocyanate

The reaction was carried out in anhydrous ethyl acetate using 0.5 wt% dibutyltin diacetate (based on total solution) as the catalyst. The reaction was monitored by IR by following the disappearance of the isocyanate absorption band at 4.41 μ . The equivalent weights calculated from the reaction profiles are:

Grams/mole

299
290

Average: 295

Hydroxyl Band Absorption Measurements in Ethyl Acetate

Equivalent weights of the 3M polymer were also calculated from the intensity of the hydroxyl absorption band in ethyl acetate by relating the absorption intensity to a calibration of butanol in the same solvent. The equivalent weights determined by this method were 355 and 345 g/mole based on two determinations. The discrepancy between the two equivalent weight methods probably reflects differences in the absorption coefficients between the hydroxy group of the butanol and the prepolymer.

9.3. Functionality

Based on the molecular weight measurements ($(M_n)_o = 1240$) and equivalent weight measurements by the two methods discussed above the overall functionality of this prepolymer is:

$$f = \frac{1240}{350} = 3.5; \quad \frac{1240}{295} = 4.2$$

The spread in the calculated functionalities reflects the difference in the equivalent weight determinations. These numbers suggest that this polymer contains significant polymer fractions with functionalities in excess of 2.0.

9.4. Functionality Distribution Measurements

Previous average functionality measurements of the total polymer had indicated that this polymer lot contained significant polymer fractions with functionalities in excess of 2.0. This has been confirmed by fractionation studies on activated silica gel using Freon 113 as the initial column substrate. The polymer is deposited on the column from a Freon-113/ether solution and subsequently eluted from the column by solvent mixtures of Freon-113 and ether of progressively higher ether content. Total polymer recovery was 90%. The remaining 10% could not be recovered presumably because of their high functional group content.

Fractionation parameters and analytical data of the isolated polymer fractions are summarized below:

Identification: 416-41
 Silica gel/polymer ratio: 133/1
 Polymer charged to column: 0.980 g
 Total polymer recovery: 89.6%

<u>Fraction</u>	<u>Wt.% of Total</u>	<u>Equivalent Weight*</u> <u>(grams/mole of OH)</u>	<u>(Mn)_o **</u>	<u>Functionality</u>
I	0.7	no OH band	--	0
II	6.9	903	980	1.08
III	16.7	496	1120	2.26
IV	24.0	325	960	2.95
V	23.7	363	1500	4.13
VI	17.6	434	1630	3.76
	<hr/> 89.6%			

* by infrared measurements of the hydroxyl band in ethyl acetate.

** by VPO in ethyl acetate at 37°C.

The elution profile is shown in Figure 50. Infrared spectra of the total polymer and fractions I through VI are shown in Appendix B-9. Fraction I which is nonfunctional and which accounts for 0.7% of the total polymer, exhibits a distinctly different spectrum from that of the total polymer. Also fraction VI shows an absorption band in the carbonyl region (5.95 μ) which is not present in the other fractions.

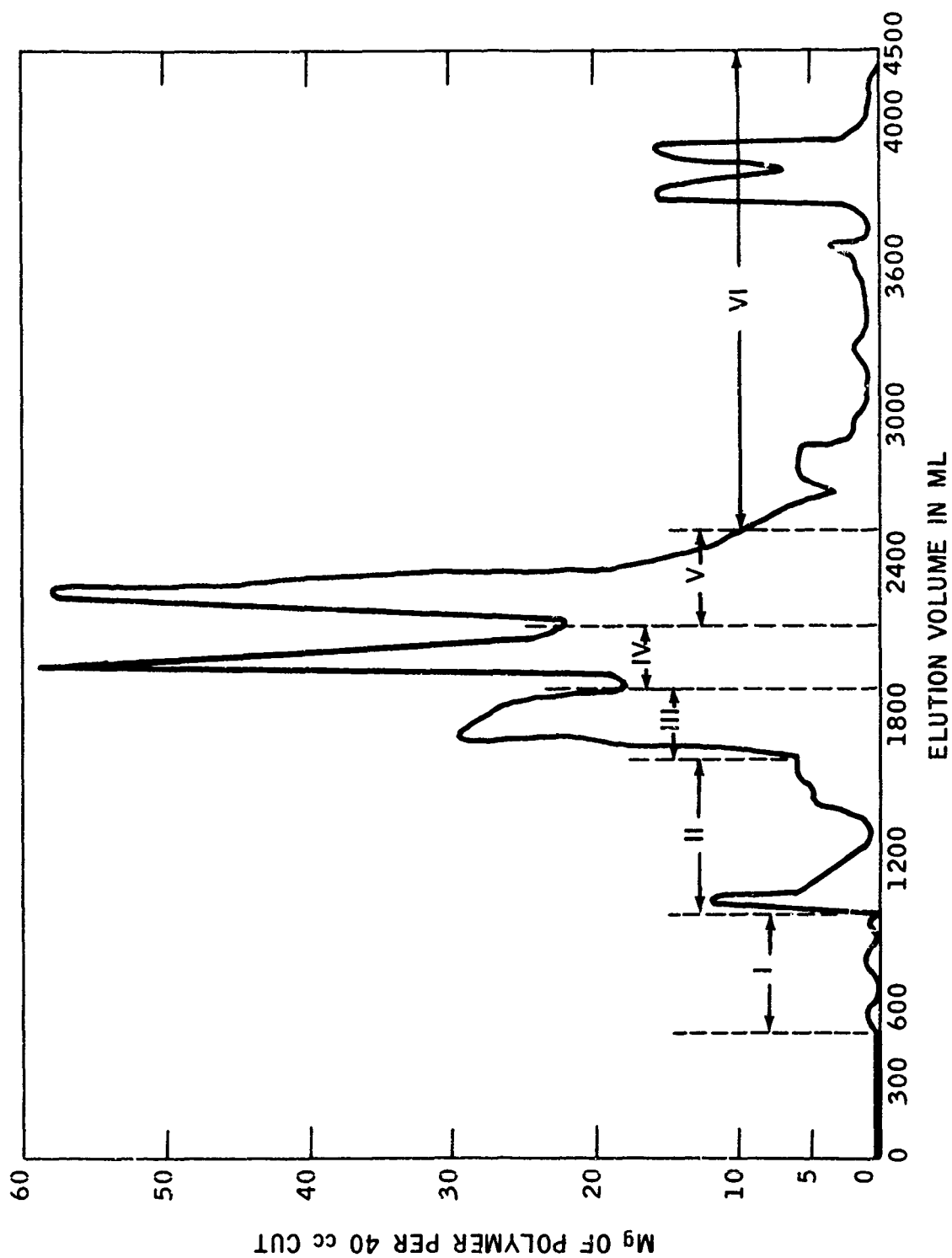


Figure 50. Fractionation of 3M's hydroxy-functional perfluoroalkylene oxide prepolymer by stepwise elution from silica gel; profile of fractionation 416-41, silica gel/polymer ratio = 133/1.

The above data clearly show that the perfluoroalkylene oxide prepolymer has a wide distribution of functionalities, extending from zero to at least four. In fact the bulk of the polymer (>65%) has a functionality of 3 or above. The polymer is therefore not simply hydroxy-terminated but obviously has hydroxy-functional groups along the chain. The approximate functionality distribution as shown graphically in Figure 511s as follows:

<u>Wt. %</u>	<u>Functionality</u>
<1%	0
7	1
17	2
24	3
41	4
remaining 10%*	4 or >4

* could not be desorbed from the column

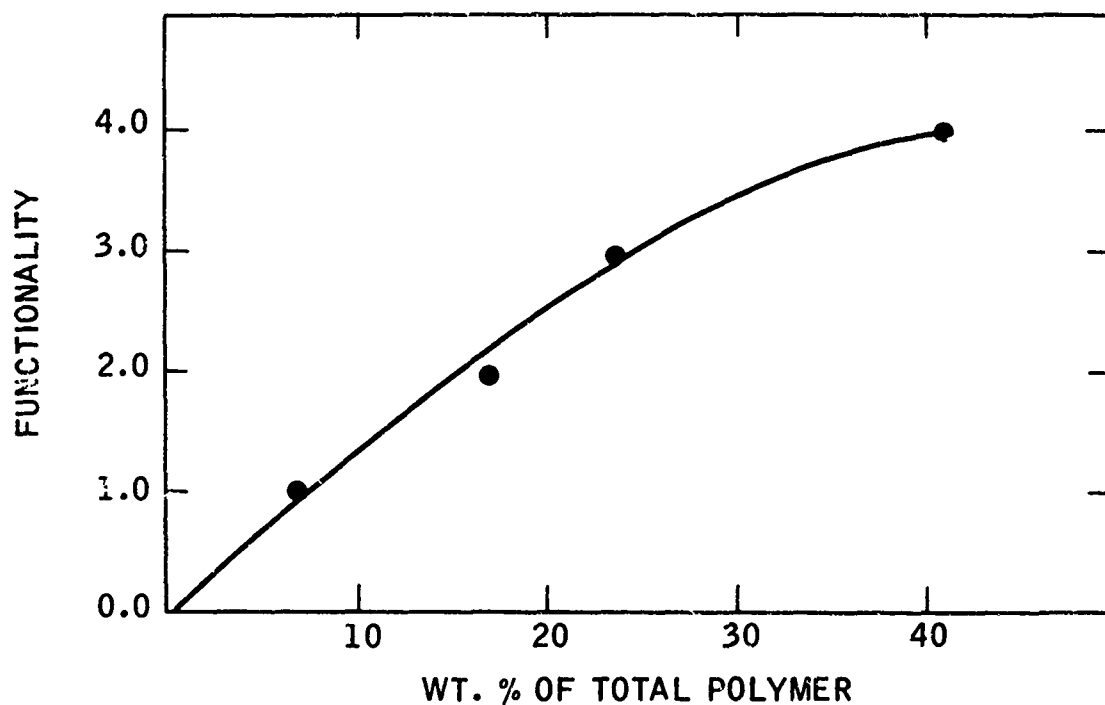


Figure 51. Functionality distribution of 3M's hydroxy-functional perfluoroalkylene oxide prepolymer.

10. COOH-BUTAREZ, TYPE II,
LOT 2285

The carboxy-functional Butarez is a polybutadiene prepolymer prepared by the Phillips Petroleum Company. A sample of this prepolymer, lot 2285, was received from the Air Force Rocket Propulsion Laboratory for functionality and functionality distribution measurements.

10.1. Molecular Weight Measurements by VPO

Prior to molecular weight measurements the prepolymer was vacuum stripped at 40°C to constant weight. The weight loss (% volatiles) based on four separate samples was 2.5 to 2.6 wt.%. Number average molecular weight measurements of the stripped polymer by VPO in chloroform at 37°C showed a strong negative concentration dependence of molecular weight. Additional molecular weight measurements were subsequently carried out in o-dichlorobenzene at 130°C in the hope that the strong negative concentration dependence would be eliminated at the higher temperature. Figure 52 shows the concentration dependence of molecular weight in the above two solvent-temperature systems. Both systems show identical concentration dependence of molecular weight; the apparent molecular weight increases with decrease in concentration. Least square analysis of the data resulted in an extrapolated molecular weight of $(M_n)_0 = 4500$.

10.2. Equivalent Weight Measurements

The COOH-equivalent weight of this prepolymer sample was determined in duplicate by potentiometric titration with 0.1 N tetrabutyl ammonium hydroxide:

Equivalent Weight
(Grams/Mole COOH)

2714

2706

Average: 2710 grams/mole

This value agrees with Aerojet's analysis of January 2, 1967, (0.037 equiv/100 g = 2700 g/mole).

In order to be able to determine the equivalent weight of small polymer fractions, we set up an infrared calibration based on the Butarez polymer. Figure 53 relates the intensity of the carbonyl absorbance at 5.8μ to the concentration of Butarez in tetrahydrofuran solution. From the intensity of the carbonyl absorption band of prepolymer fractions of known concentration, the equivalent weight can be calculated.

FIGURE 52

CONCENTRATION DEPENDENCE OF MOLECULAR WEIGHT
FOR BUTAREZ CTL, IN CHLOROFORM AT 37°C
AND O-DICHLOROBENZENE AT 130°C

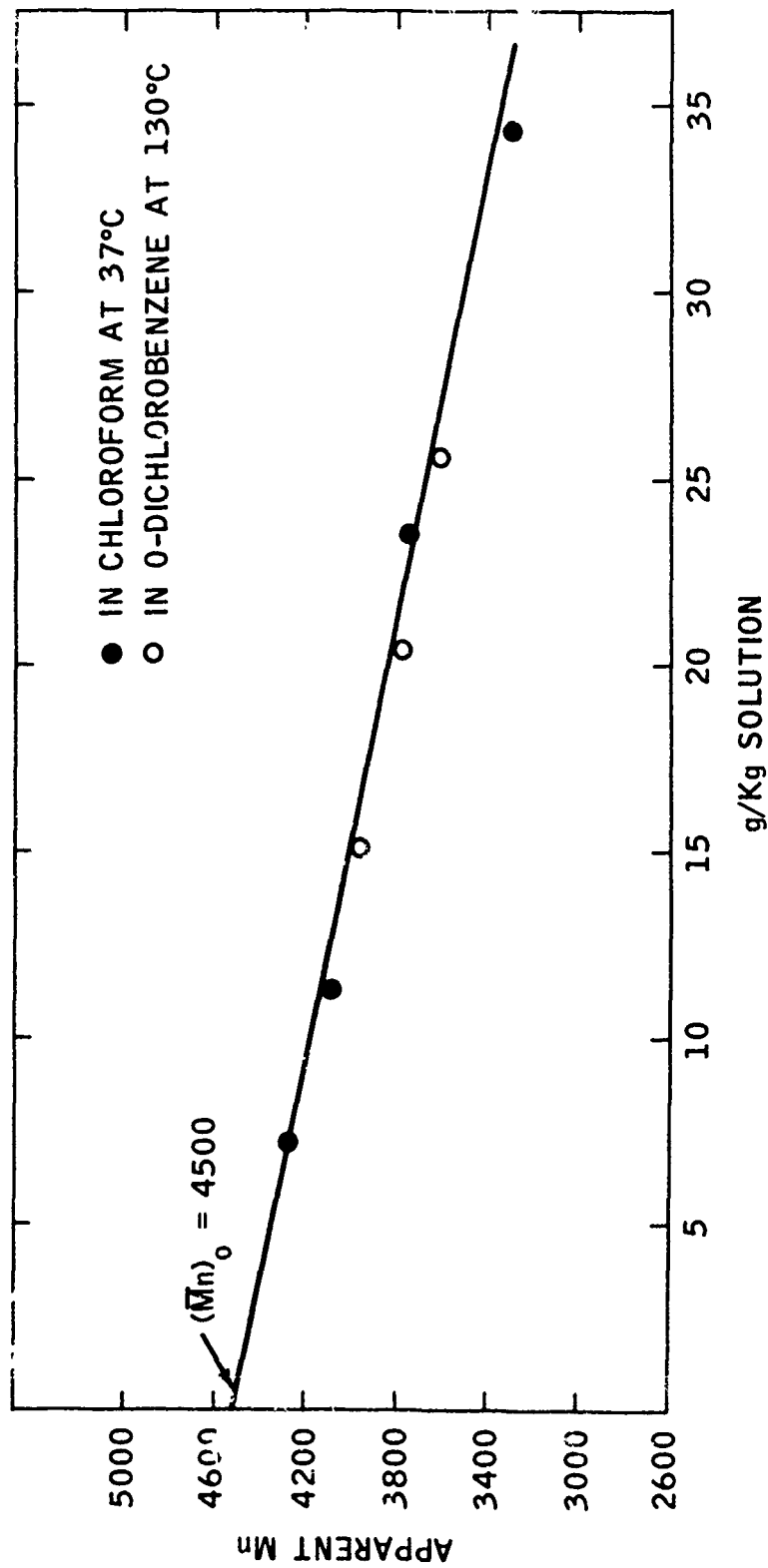
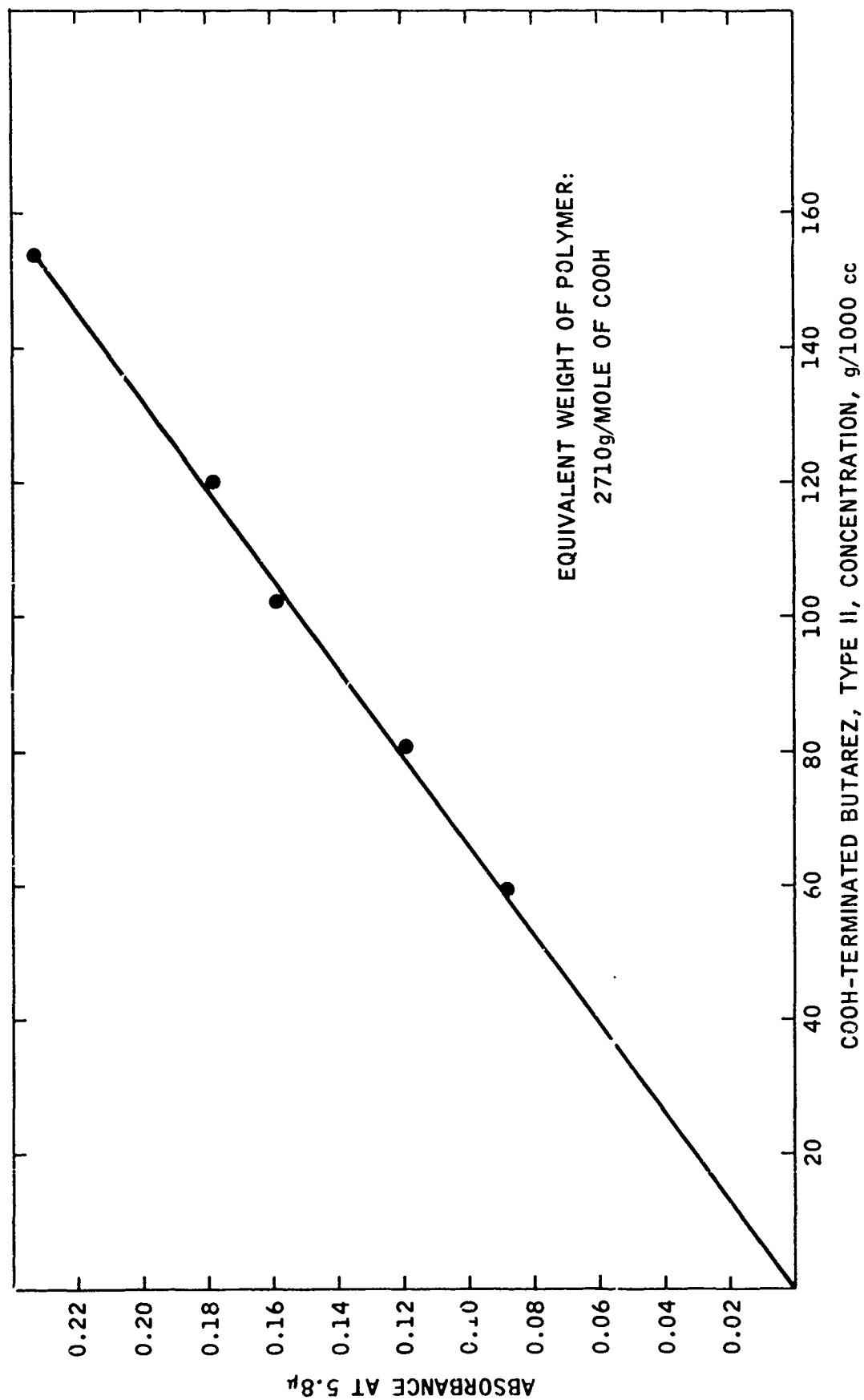


Figure 53

CORRELATION OF CARBONYL ABSORBENCE WITH POLYMER CONCENTRATION
FOR BUTAREZ CTL, LOT 2285, IN TETRAHYDROFURAN



10.3. Functionality

The average functionality calculated from molecular weight measurements in chloroform and equivalent weight measurements by potentiometric titration is:

$$f = \frac{4500}{2710} = 1.66$$

This value is significantly below the theoretical functionality of 2.0. It should be realized, however, that the presence of 1.0% antioxidant in the prepolymer suppresses the number average molecular weight and therefore gives an apparently lower functionality.

Fractionation studies were subsequently carried out to determine the functionality distribution of Butarez CTL, type II.

10.4. Functionality Distribution

COOH-terminated Butarez, lot 2285, was fractionated by stepwise elution from silica gel using the procedure previously described for the fractionation of COOH-Telagen-S. This is the first unsaturated prepolymer we have attempted to fractionate by functionality under this program using the stepwise elution technique previously developed for saturated COOH and OH-terminated prepolymers. Initial fractionation studies were carried out at silica gel/polymer ratios of 26/1 and 108/1 respectively.

At each of these ratios a certain amount of polymer was nonadsorbed and was immediately eluted from the column. Infrared spectra showed that these fractions contained COOH-functionality. The reason for their non-adsorbance on the gel therefore was not a lack of functional groups (that is nonfunctional polymer). It therefore appeared that the reason for non-adsorbed polymer was an insufficient ratio of silica gel to polymer. We have therefore carried out two additional fractionations at higher gel/polymer ratios, and as a result the nonadsorbed polymer fraction was reduced to zero. The dependence of the amount of nonadsorbed polymer on the gel/polymer ratio is summarized below.

<u>Identification of Fractionation</u>	<u>Silica Gel/Polymer Ratio</u>	<u>% Nonadsorbed Polymer</u>
369-158	26/1	39.1
369-160	108/1	14.5
416-17	127/1	5.5
416-15	197/1	0

Apparently a silica gel/polymer ratio in excess of 130/1 is required for complete adsorption of the polymer. At these high gel/polymer ratios polymer recovery is a problem. For instance only 78 wt% of the polymer was recovered in fractionation run 417-15 (silica gel/polymer ratio = 197/1) after a total elution volume of 7 liters. Even at this high silica gel/polymer ratio the first fraction eluted from the column shows the presence of COOH-functional groups by infrared. Analysis of this fraction (I) showed that it is of low functionality (0.34), apparently a mixture of non- and monofunctional components. It is very likely that adsorption of the Butarez prepolymer on the silica gel takes place both through the functional end groups as well as through the unsaturation of the polymer backbone.

Fractionation parameters and analyses of the polymer fractions for fractionation 416-15 are summarized below:

Identification: 416-15
Silica gel/polymer ratio: 197/1
Polymer charged to column: 1.519 g
Total polymer recovery: 77.9%

<u>Fraction</u>	<u>Wt% of Total</u>	<u>(Mn)o</u>	<u>Equivalent Weight (Grams/Mole of COOH)</u>	<u>Functionality</u>
I	10.7*	3200	9430	0.34
II	15.8	4500	2680	1.68
III	9.4	4700	1860	2.53
IV	23.9	5150	2100	2.45
V	15.9	4420	2190	2.02
VI	2.2	--	--	--

* this figure includes about 1% antioxidant
(based on total polymer)

The elution profile is shown in Figure 54. Molecular weight measurements of fractions I through IV are summarized in Figure 55. All fractions showed the typical negative concentration dependence of molecular weight with concentration as previously shown in Figure 52 for the total polymer. Infrared spectra of the total polymer and fractions I through IV are shown in Appendix B-10.

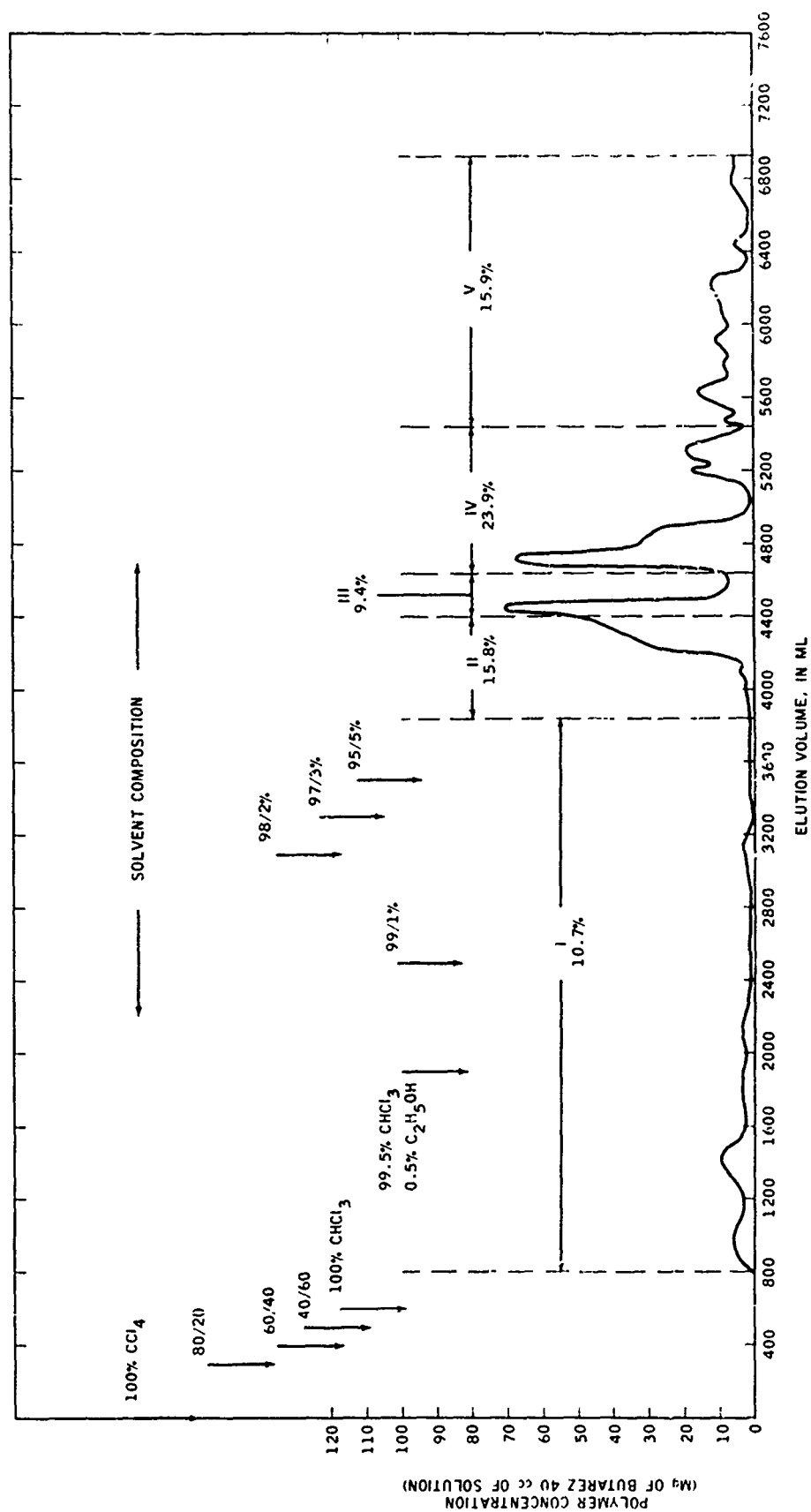


Figure 54. Fractionation of COOH-Butarez, lot 2285 by stepwise elution from silica gel; elution profile of run 416-15. Silica gel/polymer ratio = 197/1.

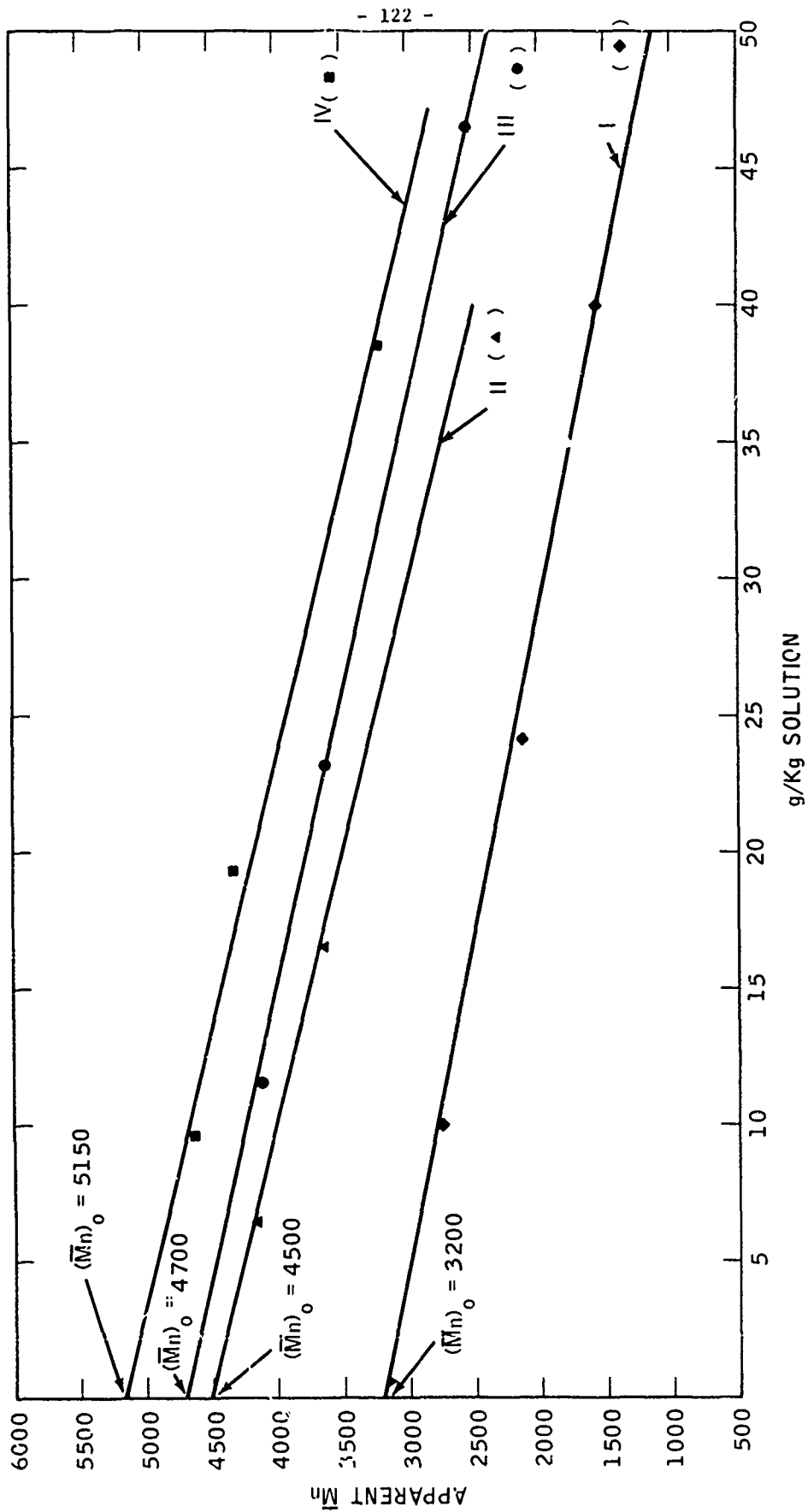


Figure 55 Concentration dependence of molecular weight for COOH-Butarez fractions 416-15-I through IV by VPO in chloroform at 37°C.

This fractionation study should not be considered a definitive study of the functionality distribution of COOH-Butarez, type II, because of the difficulty encountered in quantitatively desorbing the polymer. However, certain conclusions can be drawn. Fraction I which accounts for 10.7 wt% of the total polymer is clearly of low functionality (0.34). It is apparently a mixture of non- and monofunctional polymer. About 1% anti-oxidant was separately isolated but is included in the above figure of 10.7%. Fraction I is therefore composed of 9.7% prepolymer of functionality 0.34 and about 1% antioxidant. Fraction II which accounts for 15.8 wt% of the total Butarez polymer has a functionality of 1.68. This figure suggests that fraction II is a mixture of mono- and difunctional prepolymer. An approximate breakdown of this fraction based on its functionality of 1.68 is 4-5% monofunctional and the remainder difunctional. The total content of non- and monofunctional prepolymer is therefore $>10\%$ $<15\%$. Fractions III and IV have an apparent functionality of 2.53 and 2.45 respectively. The apparent presence of components having more than difunctionality should be viewed with scepticism at this point. It has been our experience with other polymers in the past that components having more than difunctionality are eluted from the column only after all difunctional material has been eluted. It should be noted that fraction V is strictly difunctional, therefore raising doubt as to the validity of the high functionality of fractions III and IV. We do not consider these data, therefore, as being evidence of the presence of components having functionality greater than two. Nevertheless the question of the presence of polymer components having greater than difunctionality has been raised and needs further studies.

11. SINCLAIR'S POLY B-D,
A HYDROXY-FUNCTIONAL POLYBUTADIENE

Functionality and functionality distribution measurements have also been carried out on two samples of Sinclair's Poly B-D, a hydroxy-functional polybutadiene. This polymer is of potential interest as a propellant binder because of its reportedly higher functionality. It is available in two different molecular weight levels, designated R-45M and R-15M.

11.1. Molecular Weight Measurements

Number average molecular weight measurements were obtained by VPO in chloroform at 37°C. As shown in Figures 56 and 57 both polymers show a negative dependence of apparent molecular weight with polymer concentration. The extrapolated molecular weights $(\bar{M}_n)_0$ are summarized below.

<u>Polymer Sample</u>	<u>$(\bar{M}_n)_0$</u>
Poly B-D, R-45M	2770
Poly B-D, R-15M	3420

11.2. Equivalent Weight Measurements

Equivalent weight measurements were carried out on both the lower and higher molecular weight Poly B-D. Equivalent weights were determined by reacting the polymer with toluenesulfonyl isocyanate in dilute chloroform solution. The results were:

<u>Sample</u>	<u>Equivalent Weight (grams/mole of OH)</u>
Poly B-D, R-45M (lot #803311)	1200
Poly B-D, R-15M (lot #707203)	1380

11.3. Functionality

From the number average molecular weights and equivalent weights the following functionalities were calculated.

	<u>Functionality</u>
R-45M	2.31
R-15M	2.48

On the basis of these data it was expected that both Poly B-D samples contain substantial quantities of polymer components having functionalities greater than 2. Functionality distribution measurements were therefore carried out with R-45M, the lower molecular weight Poly B-D.

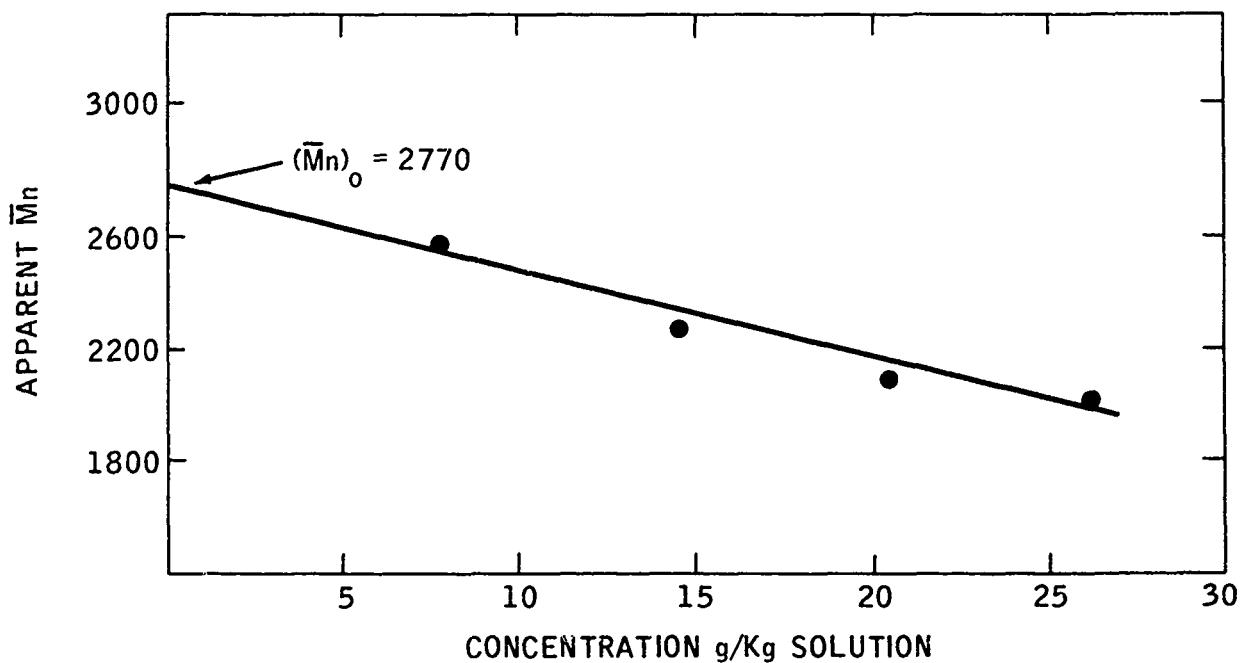


Figure 56. Concentration dependence of molecular weight for Sinclair's Poly B-D, R-45M, lot #803311, by VPO in chloroform at 37°C.

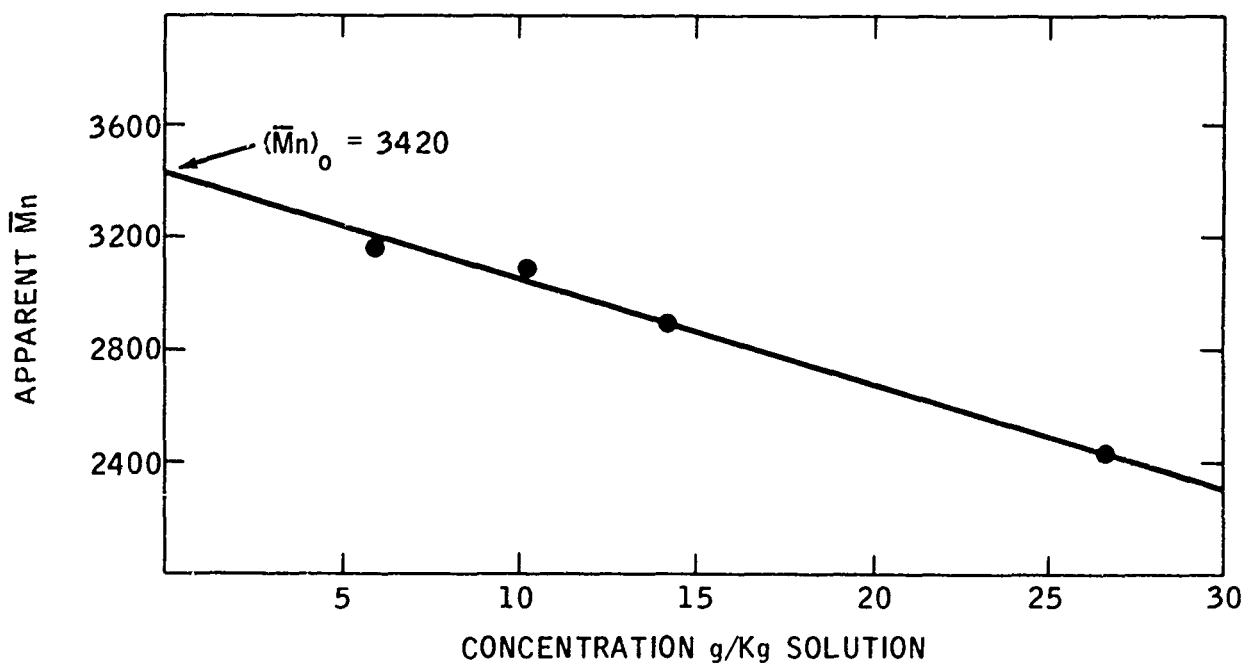


Figure 57. Concentration dependence of molecular weight for Sinclair's Poly B-D, R-15M, lot #707203, by VPO in chloroform at 37°C.

11.4. Functionality Distribution Measurements

R-45M polymer was fractionated by stepwise elution from silica gel using CCl_4 , $\text{CCl}_4\text{-CHCl}_3$ mixtures, CHCl_3 , $\text{CHCl}_3\text{-CH}_3\text{CN}$ and $\text{CHCl}_3\text{-CH}_3\text{CH}_2\text{OH}$ solvent mixtures. The elution profile is shown in Figure 58. Total recovery was 87.3%. The residual polymer is very strongly held on the gel. Analyses of the polymer fractions are summarized below:

Identification	416-145
Silica gel/polymer ratio:	44/1
Polymer charged to column:	1.698
Total polymer recovery:	87.3%

<u>Fraction</u>	<u>Wt% of Total</u>	<u>Equivalent Weight*</u> <u>(Grams/Mole of OH)</u>	<u>($\overline{\text{Mn}}$)_o</u>	<u>Functionality</u>
I	0.35	∞ **	--	0
II	10.4	2010	5380	2.68
III	7.81	1530	3800	2.48
IV	46.6	995	2300	2.31
V	9.1	700	1640	2.34
VI	7.21	770	1970	2.56
VII	5.9***			

* based on reaction with toluene sulfonyl isocyanate

** IR shows no hydroxyl band

*** open cut, recovery not complete

The above data on the functionality of individual fractions do not permit specific conclusions as to the functionality distribution of R-45M. However, the data clearly demonstrate that the functionality of R-45M is substantially in excess of 2.0.

Apparently fractionation by molecular weight has primarily taken place. It is believed that unsaturation in the prepolymer tends to interfere with the separation by functionality. This parameter requires further studies.

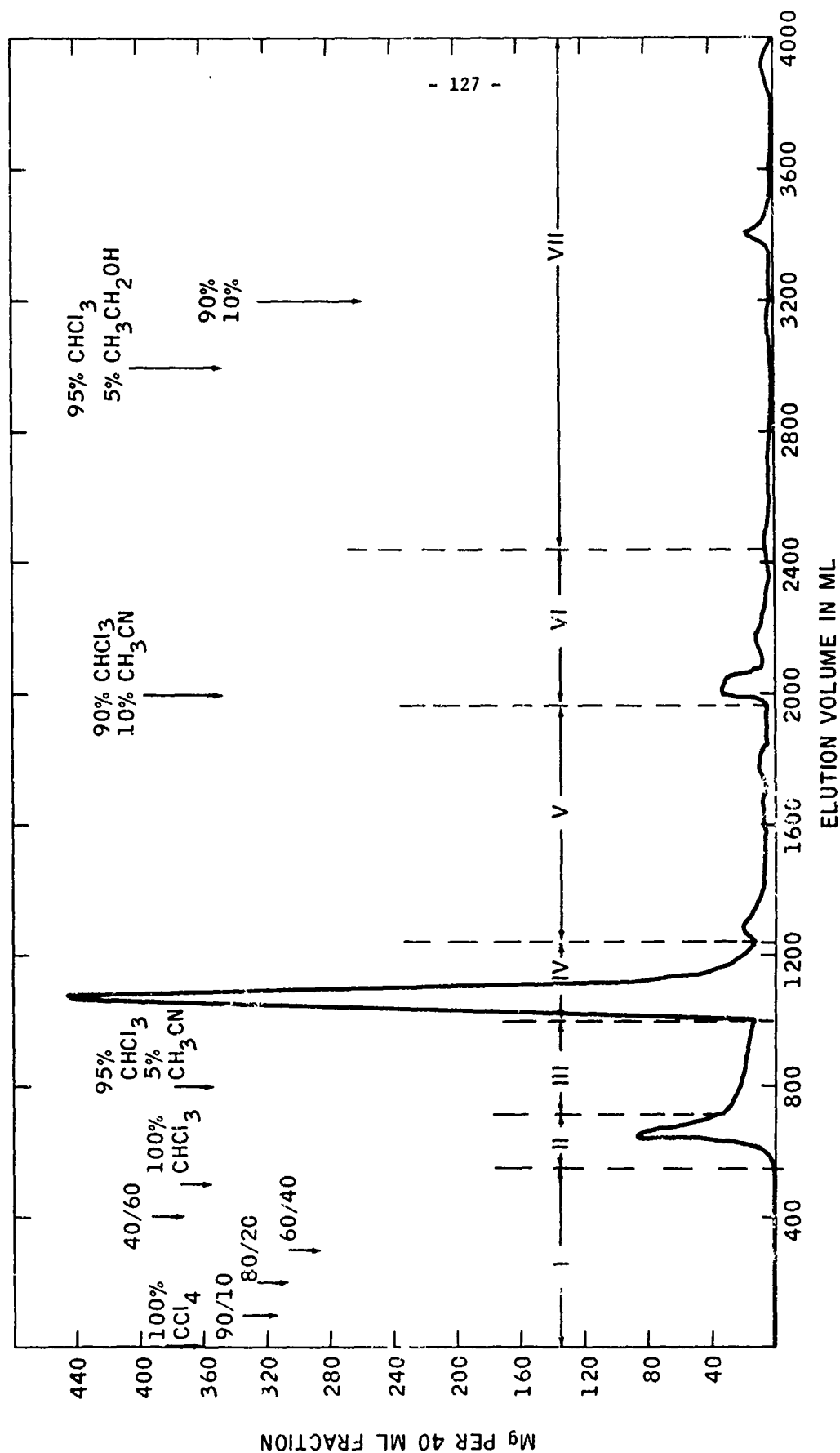


Figure 58 Elution profile for Poly B-D, R-45M by stepwise elution from silica gel.

APPENDIX A-1

MOLECULAR WEIGHT METHODS

MOLECULAR WEIGHT METHODS

A number of methods have been used for molecular weight determination. Only a few, however, are applicable to the low molecular weight range (1000-5000) which is of interest in connection with binder prepolymers. From an examination of the available methods and their limitations we selected vapor pressure osmometry (VPO) as the most suitable method for this low molecular weight range. Below is a discussion of the VPO method and other methods which were initially considered for this program.

Vapor pressure osmometry (VPO) is a thermoelectric differential vapor pressure technique for determining number-average molecular weight (M_n) of polymers. It has found widespread use for measuring molecular weights of polymers of low or moderate molecular weight (oligomers to 10,000). The thermoelectric method has significant advantages in speed and in small sample size (milligrams). The basis of the thermoelectric method is the measurement of the small temperature difference resulting from a differential mass transfer between droplets of pure solvent and polymer solution maintained in an atmosphere of solvent vapor. The net effect of this differential mass transfer gives rise to condensation of solvent on the solution drop and causes a temperature difference between the two drops. This temperature difference is proportional to the vapor pressure lowering, and hence proportional to the solute concentration. Since the vapor pressure lowering of a solute in solution is a colligative effect, dependent solely upon the number of dissolved molecules, the temperature difference can be related to the molecular weight of the solute.

A standard concentration is normally used and the apparatus is calibrated with a solute of known molecular weight. As with most colligative property measurements, the plot of readings (ΔR) versus concentration

concentration for polymers is not a horizontal line and the $\Delta R/C$ ratio must be extrapolated to zero concentration. With a good standard curve, the accuracy and reproducibility are good. Routinely, 3% reproducibility is obtained and in many instances the reproducibility is within 1-2%. Drop size and atmospheric pressure changes do not have a primary effect. Since the temperature change is extremely small and there is a limit to the degree of temperature control which can be obtained and the sensitivity of the thermistor, the practical limit of molecular weight is about 10,000-20,000.

The sensing elements of the Mechrolab Osmometer are two small thermistor beads of a resistance of about 10,000 ohms. The change in the thermistor resistance is measured with a simple DC resistance bridge, the sensitivity and stability of which permits determination of minimum increments of 0.01 ohms, equivalent to less than 0.0001°C.

The sensitivity of the VPO method also depends on the heat of vaporization of the solvent. This follows from the Clausius-Clapeyron equation:

$$\frac{dP}{dT} = \frac{\Delta H_v}{T\Delta V}$$

where $\Delta V = V_g - V_l \approx V_g$

and from the ideal gas law

$$PV = nRT$$

$$V = \frac{RT}{P} \quad n = 1 \text{ since } \Delta H_v \text{ is the molar heat of vaporization}$$

hence

$$\frac{dP}{dT} = \frac{\Delta H_v P}{RT^2}$$

or

$$\frac{dP}{PdT} = \frac{\Delta H_v}{RT^2}$$

hence

$$d \ln P = \frac{\Delta H_v}{RT^2} dT$$

$$\text{and} \quad \Delta T = \frac{RT^2}{\Delta H_v} d \ln P$$

Osmodialysis

An average molecular weight can be calculated from the distribution information obtained by osmodialysis. Since the method yields distribution data primarily, details of the method are given in Appendix A-5.

Ebulliometry depends on colligative properties and involves the measurement of boiling point evaluation.

Raoult's law states that the reduction of the vapor pressure of a pure solvent by added solute is proportional to the molar concentration of the solute. The boiling point is therefore raised. A constant is obtained as in cryoscopy for a given solvent.

$$\text{Ebulliometric Constant } K_b = \frac{RT^2}{1000\Delta H_v}$$

Where K_b is in degrees per mole per 1000 grams

R is the usual gas constant

T is the boiling point of the pure solvent in degrees K

ΔH_v is the heat of vaporization in calories per gram

This method also requires an excellent temperature sensing device in order to get reproducible results. Many types of thermometers such as multiple junction thermocouples, matched thermistors, or platinum resistance thermometers have been used. Various systems have been used to prevent superheating, to thermostat and to condense vapor. Sintered glass particles are usually attached to the wall of the boiler to give a better boiling. Various other precautions must be taken for good results.

- The apparatus must be cleaned well before using.
- It is usual to check the atmospheric pressure for variation since this will alter the readings.
- The reading galvanometer should have temperature control and moisture control.
- The solvent must be very pure for accurate results.

The ebulliometric method for determining number-average molecular weight has been successfully applied to molecular weight in the 30,000 to 40,000 range. Among these are the work of Ray (3) and Smith (4), who reported molecular weights in the 30,000 to 40,000 range and Glover and Stanley (5) who reported precision values for molecular weights as high as 35,000 and molecular weight values up to 75,000 without giving precision. Lately Zichy (6) reported determination of molecular weights of 50,000 with 90% confidence limits of 5-10% and of 100,000 with 90% confidence limits of 10-15%. Very recently Glover (7) measured the molecular weights of narrow distribution polystyrenes, made available by the National Bureau of Standards. The molecular weights of these polymers were 170,000.

The advantages of the method are that it is relatively rapid; the apparatus is inexpensive and easy to find; the repeatability is usually 10% in ordinary apparatus but about 2% in special set-ups; the apparatus is somewhat self thermostated and exact external control is not as necessary as in other methods; and the sample size is small. The method is very applicable to the low mol. wt. prepolymer range. The method is rigorous in theory and gives an absolute mol. wt. Gel does not have a large effect. Various solvents can be used and the polymer structure and chemistry do not have an effect.

(3) Ray, N. H., Trans Faraday Soc., 48, 809 (1952).

(4) Smith, H., Trans Faraday Soc., 52, 406 (1956).

(5) Glover, C. A., and R. R. Stanley, Anal. Chem., 33, 447 (1961).

(6) Zichy, E. L., Techniques of Polymer Science, Society of Chemical Industry, Monograph No. 17, Gordon and Breach, New York, 1963.

(7) Glover, C.A., and J. E. Uirn, Polymer Letters Vol. 3, 27-29 (1965).

The method has the disadvantage that it does require boiling which usually involves high temperatures. However, in many cases low boiling solvents, such as acetone, can be used which eliminates this problem. As in cryoscopy, traces of residual solvent are bad as is moisture. There is a possible problem of association of the H bond type but this is felt to be less than with the cryoscopic method, due to the higher temperature.

This method was considered as a back-up for the VPO method.

Cryoscopy is a traditional method for determining M_n . It is one of the colligative properties like osmosis and ebulliometry and depends upon the lowering of the freezing point of a solvent by the introduction of a polymer. The method is particularly suited to the low molecular weight species contrary to osmometry.

The method requires a very good method of measuring the temperature. The better the method, the better the reproducibility. Also many other precautions must be taken such as:

- Prevention of errors due to atmosphere by using N_2
- Prevention of weighing errors
- Prevention of evaporation
- Temperature control of the cryoscope and measuring device
- Prevention of supercooling
- Prevention of molecular association
- Prevention of solid solutions

The method is in principle an absolute method but as usual a standard is normally used to obtain the cryoscopic constant for the solvent.

$$\text{Cryoscopic Constant } K = \frac{RT^2}{1000\Delta H_f}$$

Where K is in degrees per mole per 1000 grams

R = the usual gas constant

T = the freezing point of the pure solvent in degrees K

ΔH_f = the heat of fusion in calories per gram

The cryoscopic method, with very sophisticated equipment is good in the region up to about 20,000 mol. wt., but the usual apparatus is only capable of 1-3000 mol. wt. The reproducibility varies between 10% with the usual apparatus to about 2% with extreme care and excellent equipment.

One advantage of the method is that the theory is rigorous. The equipment is relatively inexpensive and easy to get. Various solvents and temperatures can be used. The method is probably independent of structure, randomness, and 'copolymerness' although this has not been checked experimentally to our knowledge. The sample size is reasonable.

The disadvantages are that the method is time consuming to set up, to obtain the proper constants (particularly when it is necessary to change solvents for another type of polymer) and to do the actual measurements. The effect of gel is probably small, but traces of solvent are very injurious to the results. Moisture is also bad. Aerojet reports that the method is sensitive to association in solution.

Although this method may have some serious disadvantages for functional prepolymers because of potential molecular association, it was considered as a back-up for the VPO method.

A number of other molecular weight methods have been considered. These methods were discarded for the purpose of measuring low molecular weight prepolymers for one or more serious limitation. The following list gives the methods and these limitations.

- Viscosity - Affected by association, gel, configuration of the polymer and the small differences between solvent and the low molecular weight polymer solutions viscosity; not an absolute method.
- Osmometry - Not applicable to low molecular weight because of diffusion.
- Light Scattering - Too time consumint and sensitive to dirt, gel, color, moisture, and perhaps polar end groups.
- Ultracentrifugation - Too time consuming.
- Elasto-osmometry - Too time consuming and inaccurate.
- Isopiestic Method - Too time consuming.
- End Group Analysis - Not applicable to variable functionality.
- NMR, Electrical Resistance, and Torsion Pendulum - These methods are not we'll developed and offer no apparent advantage.

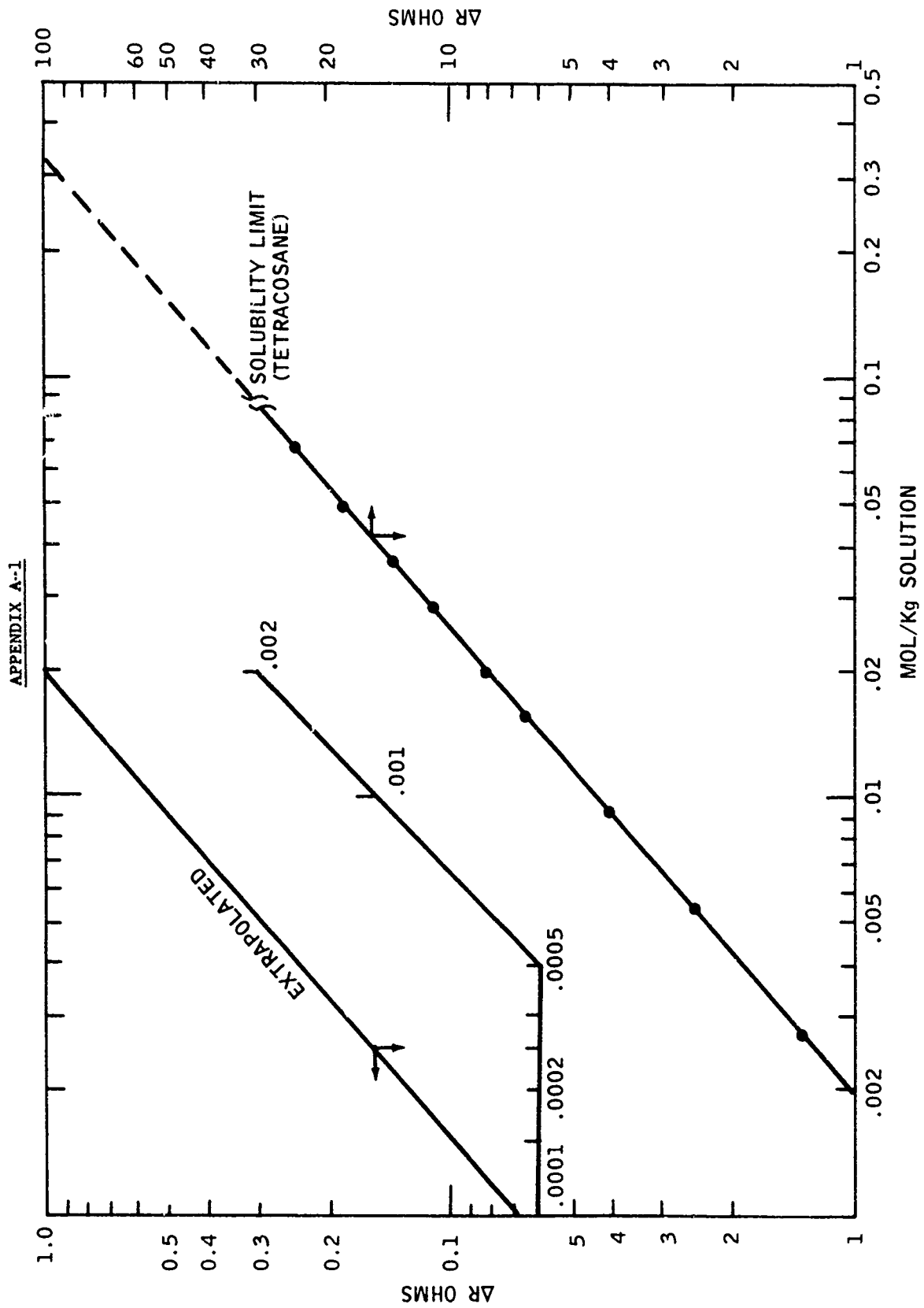


Figure 59. VPO calibration, tetracosane in 1,2-dichloroethane, logarithmic plot, showing data points upward from $\Delta R = 1$ ohm and extrapolated segment, $\Delta R < 1$ ohm

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APPENDIX A-2

EQUIVALENT WEIGHT METHODS

Equivalent Weight Methods

The number of methods which have been used for the measurement of equivalent weight are less than those for molecular weight. It is vital that the best methods be used since a good measure of functionality is dependent upon these methods as well as upon a good molecular weight determination. From an examination of the available equivalent weight methods and their limitations, we selected the following methods for this program.

The Infrared method measures the intensity of the hydroxyl stretching mode absorption of hydroxy-terminated prepolymers in solution. The success of this analysis stems from the use of a hydrogen bonding diluent (ethyl acetate or methyl ethyl ketone) which effectively eliminates the difference in OH absorption maximum wavelengths and molar extinction coefficients that are typically observed among alcohols of different molecular structure. This method has the advantage of quickness and ease and small sample size. More significantly, most of the sample can be recovered and used for other analyses.

In our analysis we have used ethyl acetate or methyl ethyl ketone as the bonding diluent and butanol as the reference alcohol. Since neither one of these two bonding diluents is a solvent for Telagen-S, we used a solvent mixture of 25 vol.% ethyl acetate and 75 vol.% carbon tetrachloride.

Figure 60 shows the total OH absorption of a series of sec-butanol reference blends in a 25 vol.% ethyl acetate/75 vol.% carbon tetrachloride solvent mixture as a function of molal concentration. The calibration was determined with the aid of a Beckman IR-8. A 0.1055 mm thick liquid absorption cell was used to measure the intensity of the absorbance. The equivalent weight of Telagen-S was determined by measuring total OH-absorption at 2.72 and 2.82 μ of Telagen-S solutions of known concentration and referring to the calibration in Figure 60.

In the case of P-BEP, OH-absorption measurements were made in methyl ethyl ketone. A new calibration line was established on the basis of n-butanol reference blends (see Figure 61). OH absorbance was measured at 2.82 microns as a function of solution concentration in the case of n-butanol reference blends. For P-BEP solutions the maximum absorption was shifted to 2.85 μ .

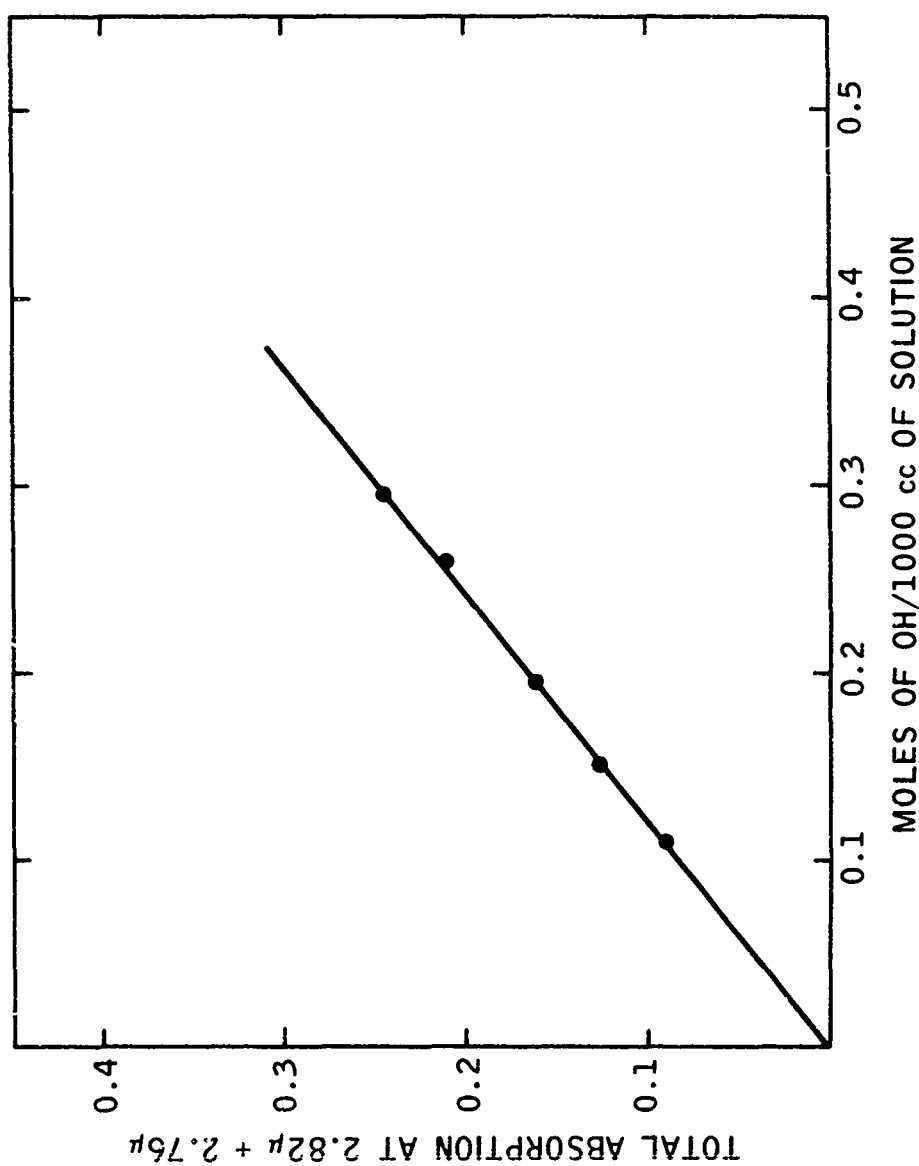


Figure 60. Calibration: sec-butanol in 25 vol.% ethyl acetate/75 vol.% carbon tetrachloride; Beckman IR-8, 0.1055 mm thick liquid absorption cell

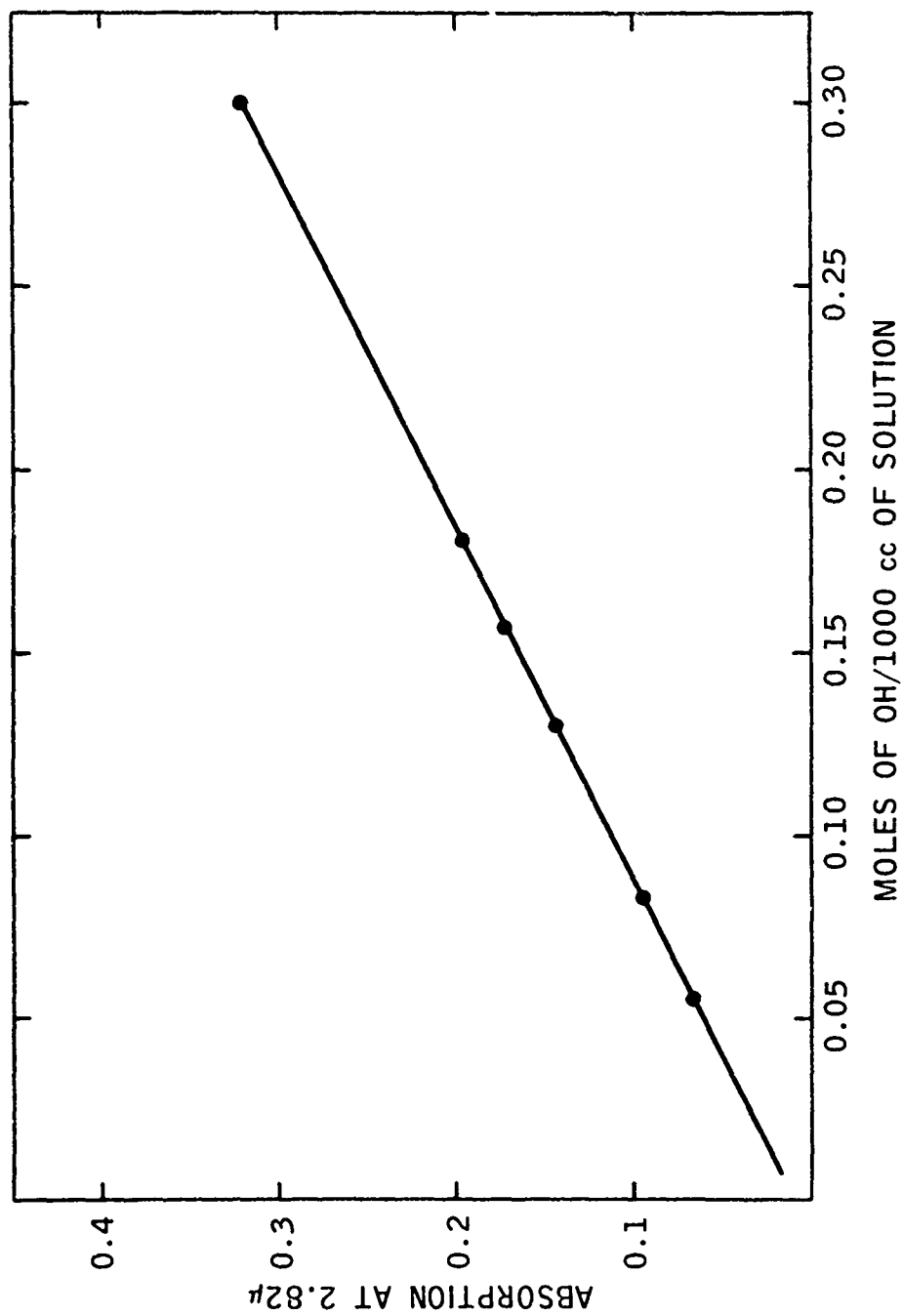


Figure 61. Calibration: n-butanol in methyl ethyl ketone; Beckman IR-8, 0.1055 mm thick liquid absorption cell

The Diborane method is a rapid and universal chemical method for the analysis of protonic end groups. The method was developed by Aerojet. Basically the method involves the reaction of Diborane with protonic material and measuring, manometrically, the evolved hydrogen.



The analysis is quite rapid, requiring about a half hour per analysis. The diborane/THF solution is commercially available. The exact concentration need not be determined. Nitro, nitrate, and other energetic groups do not interfere with the determination. Amine and carbonyl groups are also noninterfering. Moisture does interfere, since it liberates hydrogen, and it should be eliminated.

The apparatus consists of a reaction vessel with a magnetic stirrer, a serum cap and an accurate manometer. The test procedure is as follows: Excess diborane/THF solution is placed in the reaction vessel. The gas space above the solution is calibrated by injecting known amounts of n-butanol of better than 99.9% purity with a microsyringe through the serum cap and measuring the pressure resulting from the evolution of hydrogen. The volume is then calculated using the ideal gas law. The equivalent weight of polymers is determined by injecting a known weight of polymer solution and similarly recording the amount of hydrogen evolved.

Any corrections for hydrogen solubility and introduction of the polymer solution are made from standards. There are no serious disadvantages of this method except for moisture sensitivity and the fact that the material is consumed during the analysis.

In addition to the three methods discussed above, there are a series of wet chemical methods which have been used historically for this purpose. One method is based on the reaction between alcohols and anhydrides of organic acids, which is stoichiometric in the presence of pyridine. The organic acid thus liberated is bound by the pyridine to form a neutral salt. Other methods involve acetylation and saponification of the acetylated derivatives, methylation by various agents with subsequent determination of methoxy groups by the Zeisel method, acetylation with halogen anhydrides containing labeled halogen with subsequent determination of the halogen. These methods have the disadvantage that they require larger sample size, and they are sensitive to impurities.

A New Micro-Method Based on
the Reaction of Hydroxyl Group with
Toluenesulfonyl Isocyanate

Equivalent weight data obtained on P-BEP by the Diborane method differed considerably from the data obtained by the infrared absorption technique. It was, therefore, desirable to establish an independent third method for the determination of the equivalent weight of hydroxy-terminated prepolymers.

The method we have developed is based on the reaction of the hydroxyl group of the prepolymer with a reactive isocyanate. Isocyanates show a very intense absorption band at 4.4 to 4.5 μ due to the NCO stretching vibration. The isocyanate-hydroxyl reaction can, therefore, be followed spectrophotometrically (infrared) by measuring the disappearance of the isocyanate absorption as a function of time. From the known initial concentration of the prepolymer and isocyanate in solution and the amount of isocyanate reacted (as calculated from the percent decrease in NCO absorbance), the equivalent weight of the prepolymer can be calculated. This method presupposes, however, that (1) the NCO-OH reaction goes readily to completion and (2) that no significant side reactions occur which consume additional amounts of isocyanate.

Very reactive isocyanates which do not require catalysts are preferred to avoid side reactions which are known to occur with many of the common catalysts.

The intensity of the absorption band at 4.4 to 4.5 μ , assigned to the NCO stretching vibration, was measured with a Beckman IR-8, using a 0.1 mm sodium chloride cell. A base line was drawn between 3.9 to 5.0 μ .

From the IR absorption measurements and the known initial concentration of the isocyanate and polymer in solution the equivalent weight of the polymer can be calculated as follows:

If

$\left(\text{mi} \right)_{\text{NCO}}$ = the initial concentration of isocyanate in solution, in moles of NCO/100 grams of solution

w_p = the initial concentration of prepolymer in solution, in grams/100 grams of solution

$\left(A_i \right)_{\text{NCO}}$ = the initial IR absorbance of the isocyanate in solution at 4.4-4.5 μ corresponding to the initial concentration $\left(\text{mi} \right)_{\text{NCO}}$

$\left(A_f \right)_{\text{NCO}}$ = the final IR absorbance of the isocyanate in solution after the NCO-OH reaction has gone to completion

Hence at the completion of the NCO-OH reaction the fraction of isocyanate remaining is calculated from:

$\left(\frac{A_f}{A_i} \right)_{\text{NCO}}$ = fraction of isocyanate remaining

therefore

$$1 - \left(\frac{A_f}{A_i} \right)_{\text{NCO}} = \text{fraction of isocyanate reacted}$$

or upon rearrangement:

$$\left(\frac{A_i - A_f}{A_i} \right)_{\text{NCO}} = \text{fraction of isocyanate reacted}$$

Hence the number of moles of isocyanate reacted per 100 grams of solution is:

$$\left(\frac{A_i - A_f}{A_i} \right)_{\text{NCO}} \times (mi)_{\text{NCO}}$$

Since the stoichiometry of the NCO/OH reaction is 1/1 the hydroxyl equivalent weight of the polymer can be calculated from the following equation:

$$\text{Equivalent weight of polymer (in grams of polymer/mole of OH)} = \frac{w_p}{\left(\frac{A_i - A_f}{A_i} \right)_{\text{NCO}} \times (mi)_{\text{NCO}}}$$

For a rapid determination of the equivalent weight of hydroxy-terminated prepolymers a very reactive isocyanate is required. Our initial experiments have dealt with the reaction of phenylisocyanate with hydroxy-terminated prepolymers in dilute chloroform solutions. We found that the phenylisocyanate/prepolymer reaction in dilute solution at room temperature is too slow to serve as a convenient test. The addition of a catalyst such as dibutyltin dilaurate increased the reaction rate significantly. Because of the possibility of side reactions promoted by the catalyst this approach was dropped in favor of a more reactive isocyanate.

Subsequent studies were, therefore, carried out with toluene-sulfonyl isocyanate, which was found to be extremely reactive even in dilute solutions.

The rate of reaction of sulfonyl isocyanates with alcohols has been reported to be extremely fast. Ulrich (8) reports a reaction rate constant of $150 \times 10^{-4} \text{ sec.}^{-1}$ with secondary hydroxyl groups. In comparison, phenyl isocyanate has a reaction rate constant of $0.3 \times 10^{-4} \text{ sec.}^{-1}$ with secondary alcohols (9).

(8) H. Ulrich, Chem. Rev. 1965, 369-376.

(9) L. Rand, B. Thir, S. L. Reegen and U. C. Frisch, J. Appl. Polym. Sci. Vol. 9, 1787-1795 (1965).

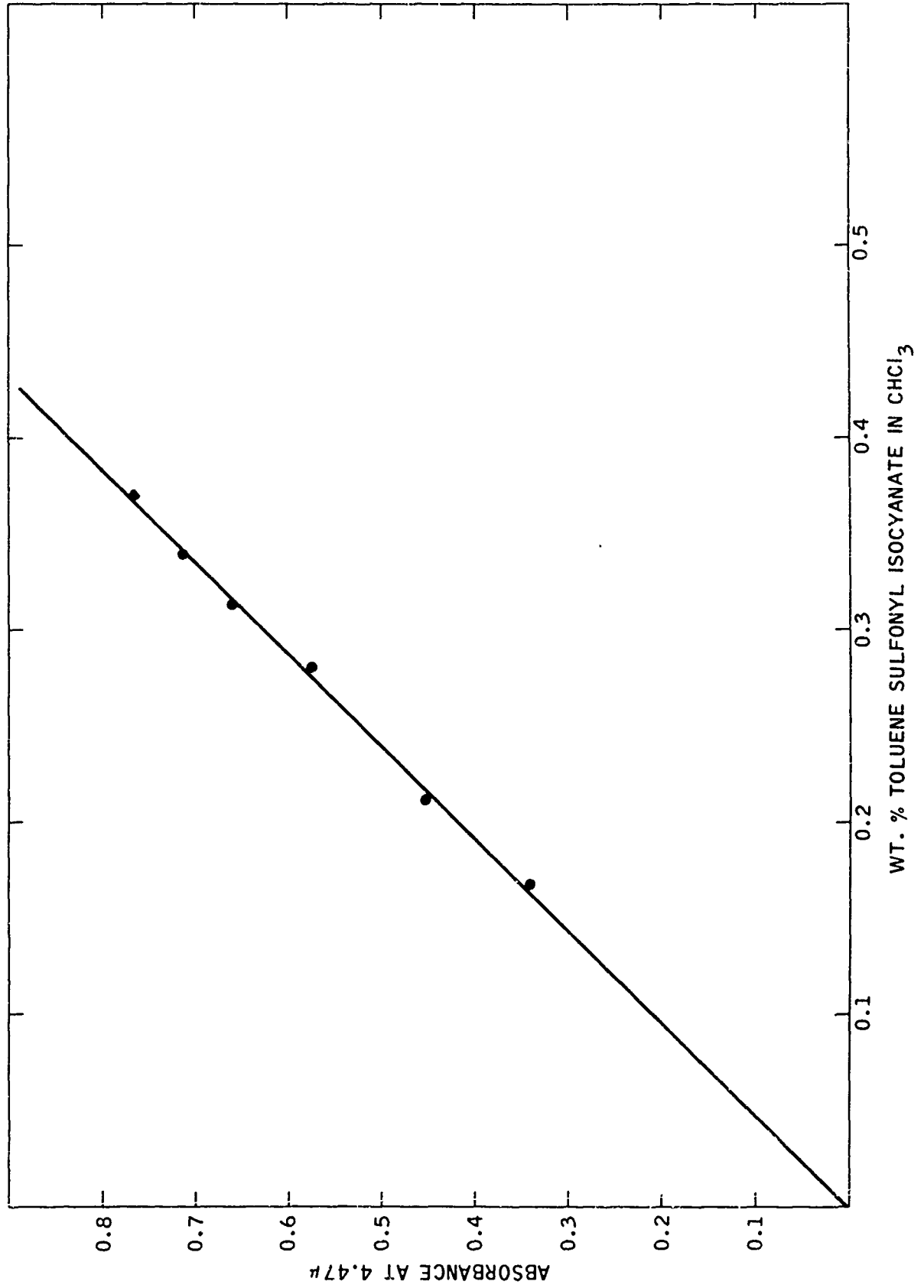
The feasibility of determining accurate equivalent weight measurements of hydroxy-terminated prepolymers by reaction with toluenesulfonyl isocyanate was checked with Telagen-S. The method was subsequently applied to P-BEP.

The isocyanate equivalent weight of toluenesulfonyl isocyanate was determined by reacting it with n-butanol of 99.9 mole % purity rather than relying on its formula molecular weight. The average of three determinations gave an isocyanate equivalent of 223.4 grams/mole of NCO.

In order to relate NCO absorbance at 4.4-4.5 μ to isocyanate concentration, a calibration plot relating NCO absorbance to wt.% toluenesulfonyl isocyanate was established. This calibration plot is shown in Figure 62.

Because of the high reactivity of this isocyanate it is absolutely essential that all solutions are prepared under dry box conditions. Furthermore, the solvent used in these experiments must be free of traces of water. The method we have adopted to insure water-free solvent is as follows: chromatography quality chloroform as received is placed in a dry box and a small amount of toluenesulfonyl isocyanate (TSNCO) is added. The TSNCO readily reacts with the water as evidenced by the decrease in NCO absorbance at 4.47 μ . The amount of TSNCO added is slightly in excess of that required for complete reaction with the water present. In subsequent equivalent weight determinations of prepolymer samples, a correction is made for the presence of the residual TSNCO in the solvent. New batches of solvent can thus be readily prepared without time-consuming treatments to remove traces of water.

Figure 62. Calibration plot of toluenesulfonyl isocyanate (TSNCO) in chloroform relating isocyanate absorbance at 4.47μ to wt.% concentration



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APPENDIX A-3

FUNCTIONALITY DETERMINATION

Functionality Determination

Functionality of a prepolymer is defined as the ratio of number-average molecular weight to equivalent weight. Functionality can therefore be calculated from separate measurements of molecular weight and equivalent weight. Functionality as calculated from number average molecular weight and equivalent weight data is greatly affected by the presence of low molecular weight nonfunctional components. Consider for example a polymer of $M_n = 2000$ and functionality of 2.0 (equivalent weight = 1000). Suppose this polymer contained 2% of a nonfunctional impurity of $M_n = 200$. The equivalent weight of this polymer is only slightly affected by the presence of the nonfunctional impurity.

Equivalent weight = 1020 grams/mole of OH. However, the molecular weight is greatly affected: $\bar{M}_n = \frac{1}{\frac{0.98}{2000} + \frac{0.02}{200}} = 1695$

The calculated functionality is then $\frac{1695}{1020} = 1.66$ when in fact, however, 98 wt.% of this polymer has a functionality of 2.0. It is therefore extremely important that nonfunctional, low molecular weight components are removed from the polymer before molecular weight and equivalent weight determinations are made.

In addition to this indirect method of functionality determination there are two principal methods for the direct determination of functionality. These are the Flory Condensation Polymer Method and the Crosslink Density Method.

Flory's original method of the reaction of bifunctional reagents using an equation modified for monofunctional species related functionality to the number average degree of polymerization:

$$\bar{P}_n = 1/2 \left(\frac{2r + f}{2r + f - 2rpf} \right)$$

Where \bar{P}_n is the number average degree of polymerization, r is the reactants ratio, f is the average polymer functionality, and p is the extent of reaction.

The equations derived by Flory are rigorous and if the experiments were carried out in the manner indicated by the equations, the functionality would indeed be obtained. However, the equations do not say anything about the actual reactions that give the condensation polymer. It is here that the central problem lies. Flory, himself, points out that the experimental difficulty of driving the reactions to even near completion is impossibly great. All the literature on condensation polymerization supports this same conclusion. Since the reactions do not approach completion, the equation can only lead to an approximation of the average functionality. In the case of OH groups, chain extended with isocyanate groups, there is the additional problem of side reactions such as allophanate formation.

In the case of the Crosslink Density Method the functionality can be calculated from the following equation:

$$\text{Crosslink Density } \bar{X}_D = \sum_{i=1}^n \frac{(f_i - 2)W_i}{f_i E_i}$$

Where f is the functionality, W_i is the weight fraction, and E_i is the equivalent weight.

This last method was improved by making a number of samples with different crosslink densities and extrapolating the functionalities so obtained to an apparent density of 0.

The same reservations raised above also apply to the Crosslink Density method. Almost no case is known where the theoretical crosslink density was found and the crosslink efficiency equal to 100%.

All of the three methods discussed above are subject to limitations. The indirect method based on number average molecular weight and equivalent weight is greatly effected by the presence of nonfunctional low molecular weight components. The Flory Condensation and the Crosslink Density Methods are subject to incomplete or side reactions.

It would appear, however, that the indirect functionality method is to be preferred, provided low molecular weight nonfunctional components are preferentially removed before molecular weight and equivalent weight measurements are made. The removal of nonfunctional components is not only necessary to arrive at a meaningful average functionality but is also essential from the standpoint of optimum mechanical properties of the cured polymer.

APPENDIX A-5

MOLECULAR WEIGHT
DISTRIBUTION METHODS

Molecular Weight Distribution Methods

Osmodialysis is a very new technique worked out in our laboratories. A paper describing the method was given at the 152nd National ACS Meeting, New York, September 1966 (10). Although the principles are not entirely new, only one reference to a closely related procedure has been found (11). Osmodialysis capitalizes on one of the limitations of ordinary membrane osmometry, namely the fact that low molecular weight species tend to diffuse through a semipermeable membrane. The method would be prohibitive in time with the old style osmometers; however, the new automated osmometers make it possible to do experiments in a reasonable time and with low manpower expenditure.

Osmodialysis is done in an automated osmometer, the Mechrolab (11). Shell-Stabin, Dohrmann, or Halikainen instruments. The method depends upon the membrane for the molecular weight range applicable. A tight membrane can be used at a low range. Ordinary gel cellulose 600 can be used in the range 25,000-500. So far, there is no limitation on solvent or polymer other than the necessity for compatibility with the membrane and instrument metals. Ionic solutes and thermodynamically poor solvents should be avoided, however.

The method can best be illustrated with a monodisperse polymer. If this polymer is dissolved in an appropriate solvent and put in the osmometer, an osmotic pressure will be recorded. This pressure is recorded as an exponential decay curve with time. If this data is replotted as log osmotic pressure versus time, a straight line results. This line is highly characteristic of the weight of polymer in solution and the molecular weight. If the molecular weight were 25,000 and no diffusion occurring, the line would be horizontal. As the polymer mol. wt. is decreased, the slope of the line becomes increasingly steep until it approaches vertical. The slope can be described by a $1/2$ and the intercept by a $t = 0$ osmotic pressure. This behavior is shown on Figure 63.

If the molecular weight of various monodisperse polymers, as known from other measurements such as Vapor Pressure Osmometry (VPO), is plotted as $\log M$ versus $\log t_{1/2}$, another straight line results. So far, all polymers appear to fall on this same line indicating that structure and chemical make-up are not very important. This is illustrated in Figure 64.

From these observations it can be seen that osmodialysis can be used to determine the molecular weight of a monodisperse solute. In order to use the method for polydisperse polymers, exponential decay theory must be used to give both an average mol. wt. and an estimation of dispersity.

(10) B. E. Hudson, Jr., ACS Polymer Preprints, 7, 467, September 1966.

(11) M. Hoffman, M. Unbehend, Makromol. Chem. 83, 292 (1965).

The type of record obtained by using a polydisperse polymer is similar to the monodisperse in osmotic pressure versus time. However, when this is plotted as log osmotic pressure versus time, a curve is formed rather than a straight line. This is illustrated by Figure 65 showing the curve obtained from a polydisperse polymer in toluene. It can be seen qualitatively that if each molecular species gives a straight line, the curve is a summation of these lines. The mol. wt. and the distribution can be obtained by an analysis of this curve.

The curve is analyzed by making use of the exponential decay law which indicates that 4 half lives reduces a given species to less than 6% of the original value. The time required for the osmodialysis measurements is 16 hours (4:30 P.M. to 8:30 A.M.). One low molecular weight distribution contributes only at 15 minutes but not after 1 hr. A second distribution contributes at 1 hr. but not at 4 hours. A third contributes at 4 hours but not at 16. And finally the highest molecular weight distribution contributes at 16 hours. Thus four distributions can be characterized in a 16 hour curve.

The actual computation of this approach is as follows. The tangent to the curve is drawn at 16 hours and extrapolated back to $t = 0$. The $t_{1/2}$ of this tangent in combination with the original plot of $\log M$ versus $\log t_{1/2}$ gives the molecular weight of this high molecular weight contributor to the total molecular weight. The arithmetical difference between the tangent and the curve is taken, and replotted. Again another tangent is drawn and the same kind of data obtained. This is repeated until the whole curve is reduced to zero.

In order to obtain the amount of each of these four fractions present in the total sample, the $t = 0$ value of the osmotic pressure as obtained from the four tangents is used. In order to use the four partial osmotic pressures, an assumption must be made which is in accord with diffusion theory and the measurements made by the original workers Staverman, etc. (12,13). This assumption is that the actual osmotic pressure is proportional to the theoretical osmotic pressure (if no diffusion were occurring) and the molecular weight.

$$\pi_{\text{act}} = \pi_{\text{theory}} \cdot k M$$

From this assumption and simple osmotic pressure theory, we can derive actual osmotic pressure as a function of the weight of polymer in solution:

$$\pi_{\text{theor}} = CRT/M \quad \text{where } C \text{ is the weight of polymer}$$

in a given volume of solution and RT stand for the usual gas constant and absolute temperature and M for the number average molecular weight.

(12) A. J. Staverman, et al., J. Poly. Sci. 23, 57 (1957).

(13) G. V. Schulz and Wo. H. Kuhn, Makromol. Chem. 29, 220 (1959).
Ibid. 50, 37 (1961).
Ibid. 50, 52 (1961).

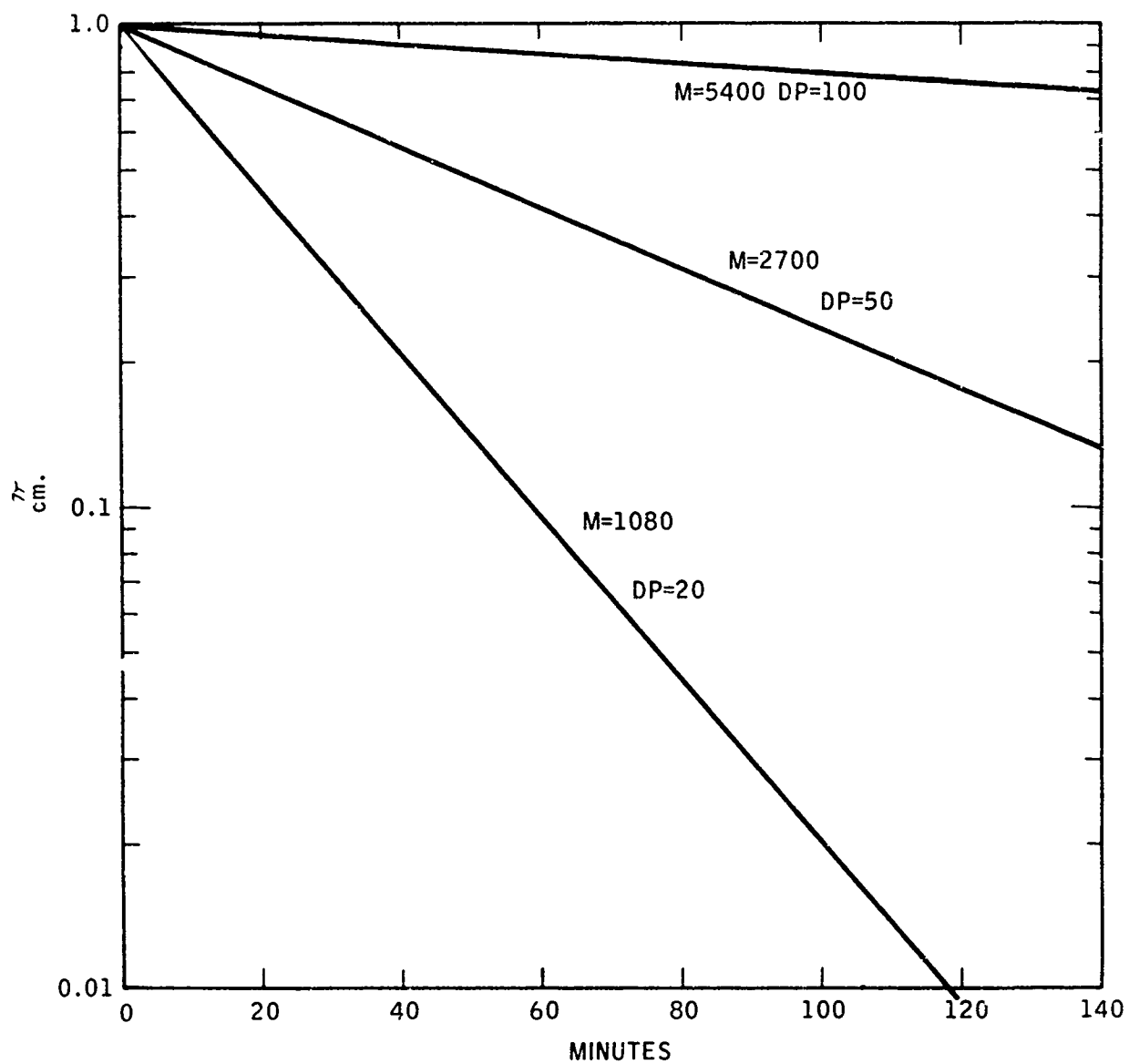


Figure 63. Log osmotic pressure (normalized) vs. time for polymers of different molecular weight

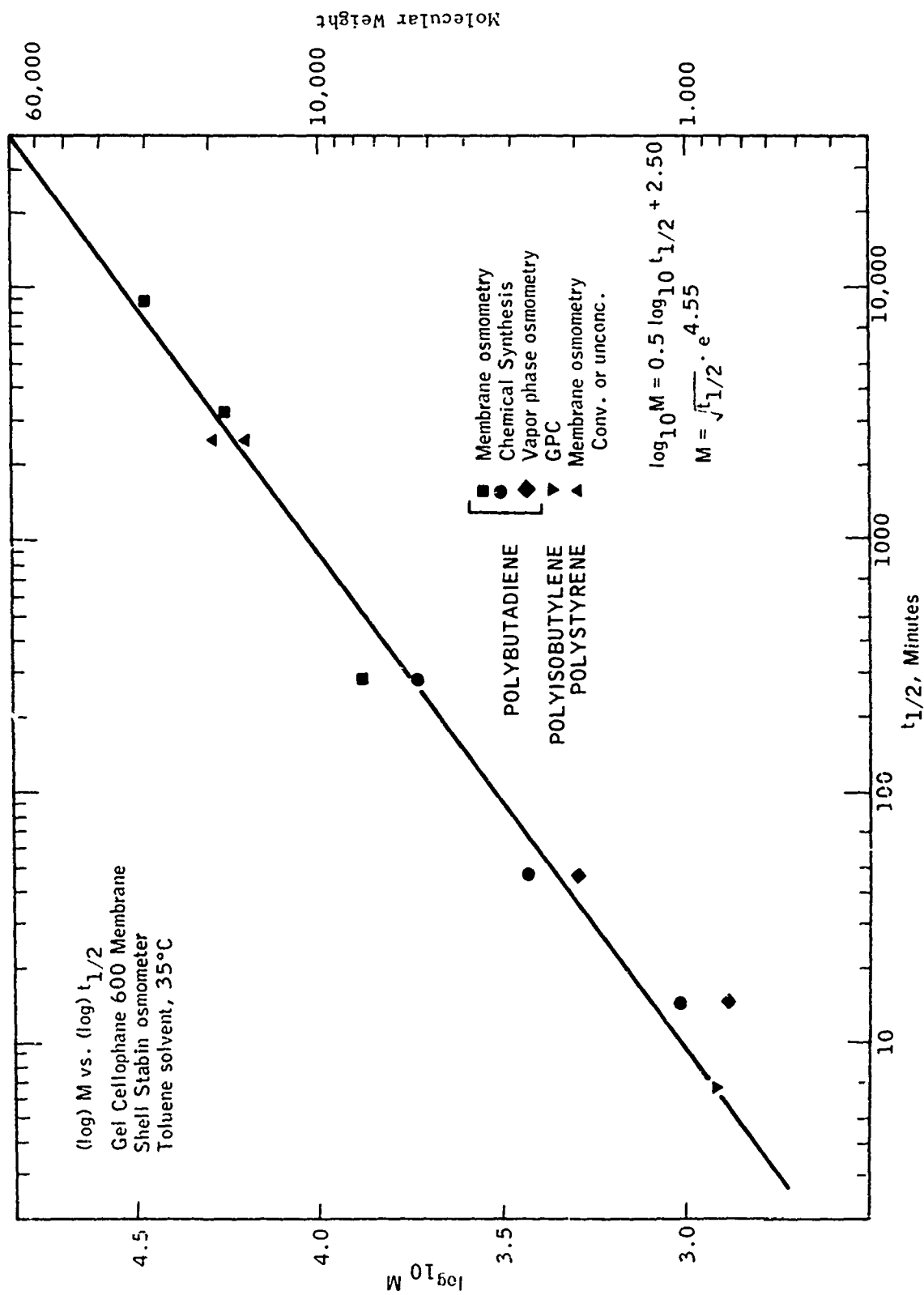


Figure 64. Osmolytic calibration

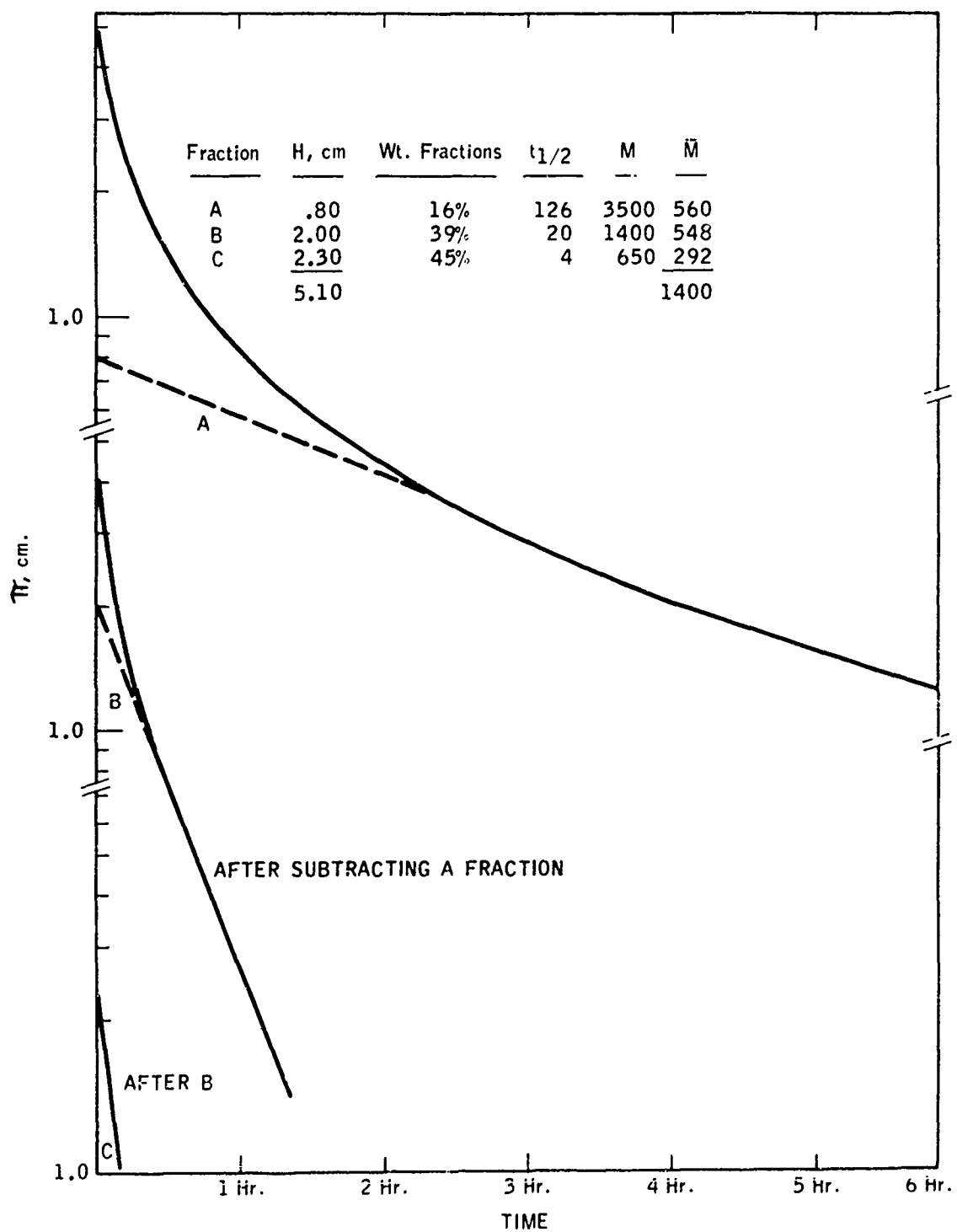


Figure 65. Log osmotic pressure vs. time for a polydisperse polymer

Since $\pi_{act} = \pi_{theor} \cdot kM$

then $\pi_{act} = CRT/M \cdot kM = CRTk$

Since RTk is constant and not a function of molecular weight, the actual osmotic pressure is a function of the weight of polymer in a given volume of solution. Also the weight fraction of a given species can be found as follows:

$$\frac{\pi_{act} \text{ (fraction A)}}{\pi_A + \pi_B + \pi_C + \pi_D} = \frac{\text{Wt. A/Vol.} \cdot kRT}{\text{Wt. A + B + C + D/Vol.} \cdot kRT}$$

$$= \frac{\text{Wt. A}}{\text{Wt. A + B + C + D}}$$

since all four species are in the same volume of solution.

In order to obtain the relative amounts of the molecular weight distributions, already calculated, the partial osmotic pressures are totaled and the total divided into each one to give a weight fraction and finally multiplied by 100 to give weight percent. Once this is done, a histogram can be constructed in which the distributions are represented by bars whose mid-point is the average mol. wt. of each and whose height is the relative abundance. From these data an average molecular weight can be calculated.

One factor with this method should be mentioned. The average calculated is believed to be $\sqrt{M_n \times M_w}$ which represents the most abundant species by weight in a normal or symmetrical molecular weight distribution. The method does not correlate with the usual number averages from VPO. Work is being done to establish the correction factor between the two averages so that they can be interconverted.

Technique	Molecular Weight Pairs						Solute 1	Solute 2
	Various Polydisperse Polymers							
Osmodialysis	5200	5250	5100	4378	5217		720	1150
VPO	3646	3487	4540	3700	3343	---		960
Formula Wt.	----	----	----	----	----		684	1202

(Solute 1 is sucrose octaacetate, Solute 2 is pentaerythritol tetrastearate)

The advantages of this method are that it yields not only a molecular weight average but an estimation of molecular weight distribution. The method is good for polymers which are not of uniform structure, composition or randomness since it does not depend upon a property like refractive index. In this way it is ideal for functionally modified polymers.

Other advantages may be mentioned with this method. The actual time spent in making the measurements and calculating the data is small. The method is easy to do, the equipment is available, low temperatures are used, and the sample size required is in the range of a few hundred milligrams. The effect of traces of solvent and dirt or gel is less than with VPO, and the distribution will not be affected at all. Moisture can alter the membrane character to some degree, but this is also a failing in other methods. There is no possibility of a reversal of high and low molecular weights and high and low functionality as has sometimes occurred with column fractionation methods.

One slight disadvantage is the total time necessary to make a measurement. The test is done in our labs overnight (16-19 hours). This does not hamper our operation and no actual work is required during that time. The method does use expensive equipment; however, many polymer characterization labs now have automatic osmometers for normal osmotic work.

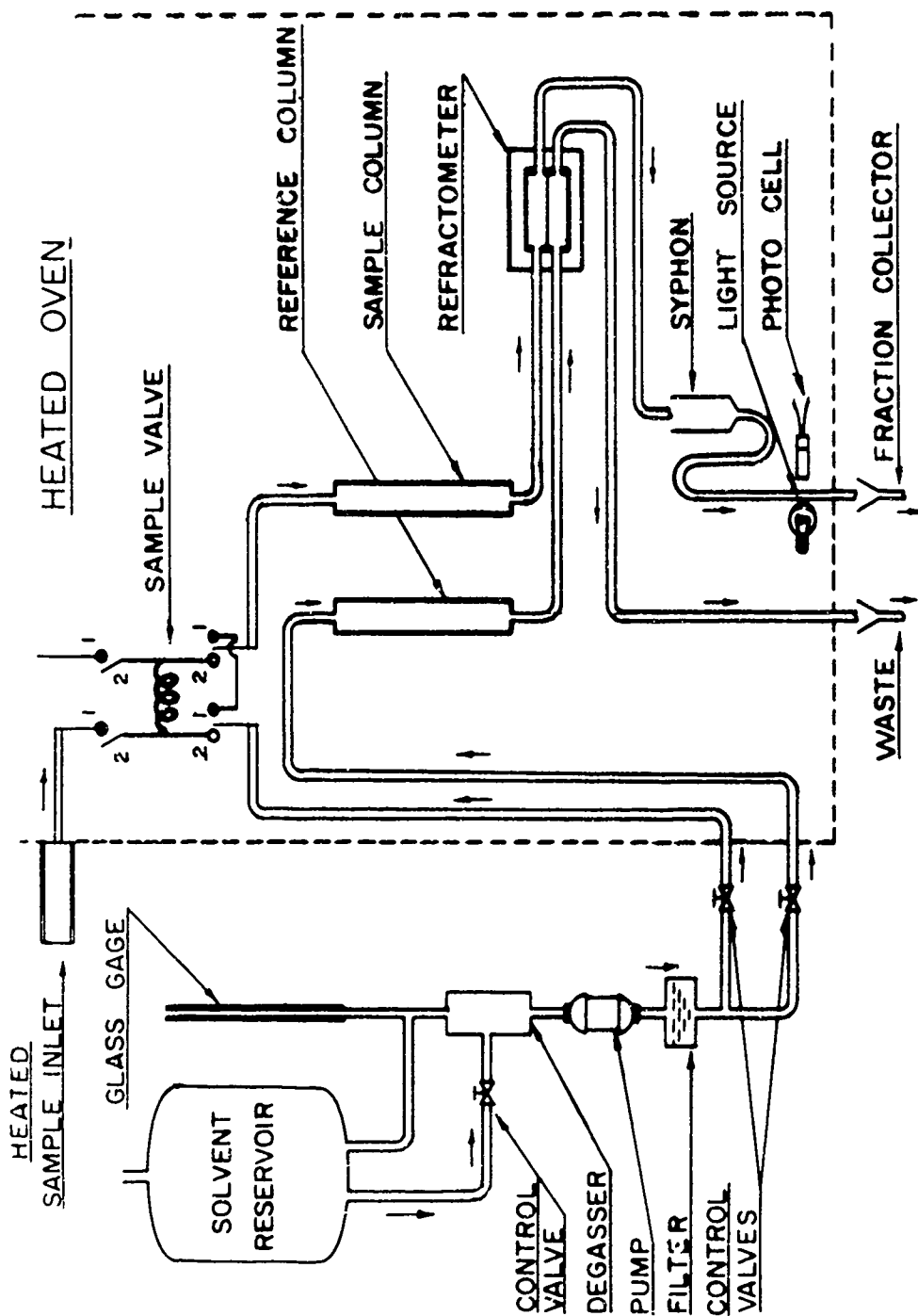
Gel Permeation Chromatography

Gel Permeation Chromatography is a type of liquid-liquid column chromatography. The stationary phase consists of a solvent-swollen gel and the mobile phase is a single solvent. The technique is of relatively recent origin, having been applied initially to the separation of water soluble biochemical mixtures. With the advent of organophilic gels and commercial equipment three years ago, the technique has experienced a phenomenal growth. The most generally used organophilic gel is a crosslinked polystyrene of controlled pore size distribution.

Application of Gel Permeation Chromatography is mainly in the area of polymer fractionation for the determination of average molecular weights and molecular weight distribution. Its advantages over conventional elution-type chromatographic fractionations are the speed and ease with which a polymer fractionation can be accomplished. A complex fractionation usually requires approximately 4 hours.

In GPC, a sample of polymer in solution is placed on a column which is packed with an inert cross-linked polymer gel and eluted with a single compatible solvent. Fractionation occurs on the basis of molecular size. This technique is therefore particularly well suited for the fractionation of polymers. Depending upon the cross-link density of the gel, molecules of different size penetrate the gel to a different degree, i.e., the residence time in the gel is different and separation occurs. Molecules larger than the maximum pore size are excluded from the gel altogether. For the fractionation of substances of a broad range of molecular weight, several columns in series containing gels of different cross-linked densities are used. By the proper choice of solvent, absorption and partition effects can be kept at a minimum, so that polymer functionality generally does not influence the separation process.

Waters Associates offers a commercial instrument, the design of which is illustrated in Figure 66. The gel is a divinylbenzene cross-linked polystyrene, developed by the Dow Chemical Company. A recording differential refractometer detects differences in refractive index between the column effluent and a reference stream of solvent.



WATERS LIQUID CHROMATOGRAPHY ASSEMBLY.

Figure 66

The refractive index differential is a direct measure of the polymer concentration in the effluent. A typical chromatogram is shown in Figure 16. Because of the small sample size (5-10 mg.), fractions cannot be collected which are large enough for further characterization. Therefore, with presently available instrumentation, the technique is applicable only to homo-polymers or copolymers of uniform structure.

It was found that the chain length of a molecule, measured in Angstroms, can be correlated with the effluent volume. The chain length is determined by considering only the valence angles and bond lengths of a fully extended linear molecule. The system is calibrated on the basis of a series of narrow molecular weight polymers, preferably of the type to be analyzed. The largest molecule emerges first and the smallest last. The simplest model of the separation process is that of a physical filtration, analogous to molecular sieve filtration. Depending on the size of a specific molecule, only a certain fraction of the internal gel volume is available for the molecule to diffuse into, so that the smaller molecules are increasingly more retarded.

Considerable support exists for the volume exclusion mechanism, although other mechanisms for the separation process have been proposed. Several models for the gel microstructure and the interaction of a macromolecule with the gel matrix have been considered. From separation studies of small molecules as well as macromolecules, there is abundant evidence that separation depends on differences in molecular volume, rather than some other molecular size parameter, such as chain length. However, a common volume parameter, which correlates elution data of all types of molecules with molecular size, has not yet been discovered.

In view of the foregoing, and for the purpose of applying gel permeation chromatography to Telagen-S, calibrations in terms of A equivalent chain length were carried out using n-paraffin hydrocarbons, whose poly-methylene backbone structure duplicates that of Telagen-S. To relate molecular weight to apparent chain length, the number-average chain length computed from the Telagen-S (whole polymer) chromatographic curve was made to coincide with the number average molecular weight determined by VPO for Telagen-S. In this manner a scale reasonably accurate as to length and position with respect to the number-average center of distribution was established for presentation of molecular weight distribution curves of Telagen-S and fractions thereof.

For application of GPC to Telagen-S, the solvent 1,3,5-tricholobenzene was used at an operating temperature of 130°C. The sample injection systems, gel columns, differential refractometer, and flow monitoring device were all at this temperature. A series of four columns designated 10^2A , 10^3A , 10^4A , and 10^5A was used. These designations, conventional with the manufacturer, Waters Associates, Inc., refer to gel porosity and indicate the approximate maximum molecular size capable of entering and being retarded by the particular column or grade of gel.

Eight pure n-paraffin hydrocarbons used to establish a molecular weight scale ranged C₉-C₉₄. This corresponds to the molecular weight range 128 to 1318. A linear plot of retention volume vs. (log) molecular weight was obtained. It was assumed that the individual molecular weight species present in Telagen-S would parallel such a calibration line. Telagen-S molecular weight distribution curves were positioned on the molecular weight scale so that M_n determined by VPO coincided with the number-average chain length computed from the distribution curves.

APPENDIX B-1

INFRARED SPECTRA OF
OH-TILLAGEN-S FRACTIONS

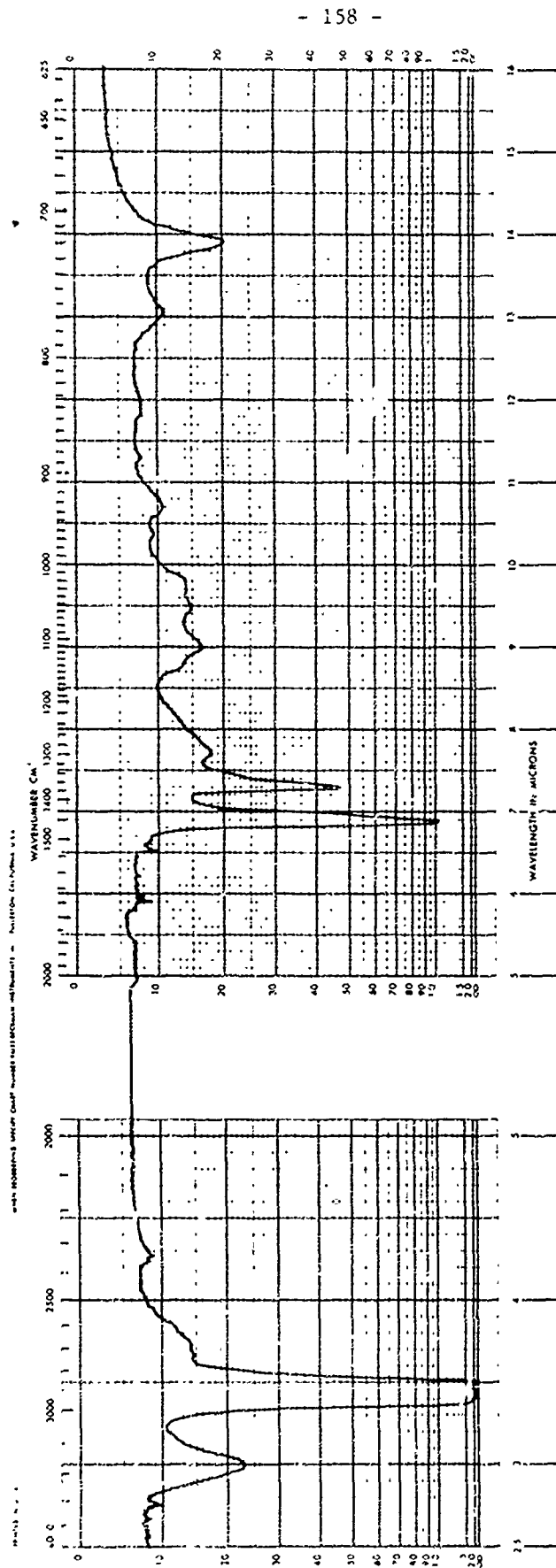


Figure 67. Infrared spectrum of OH-Telagen-S, 242 AM-148 AH, whole polymer, capillary layer between NaCl plates.

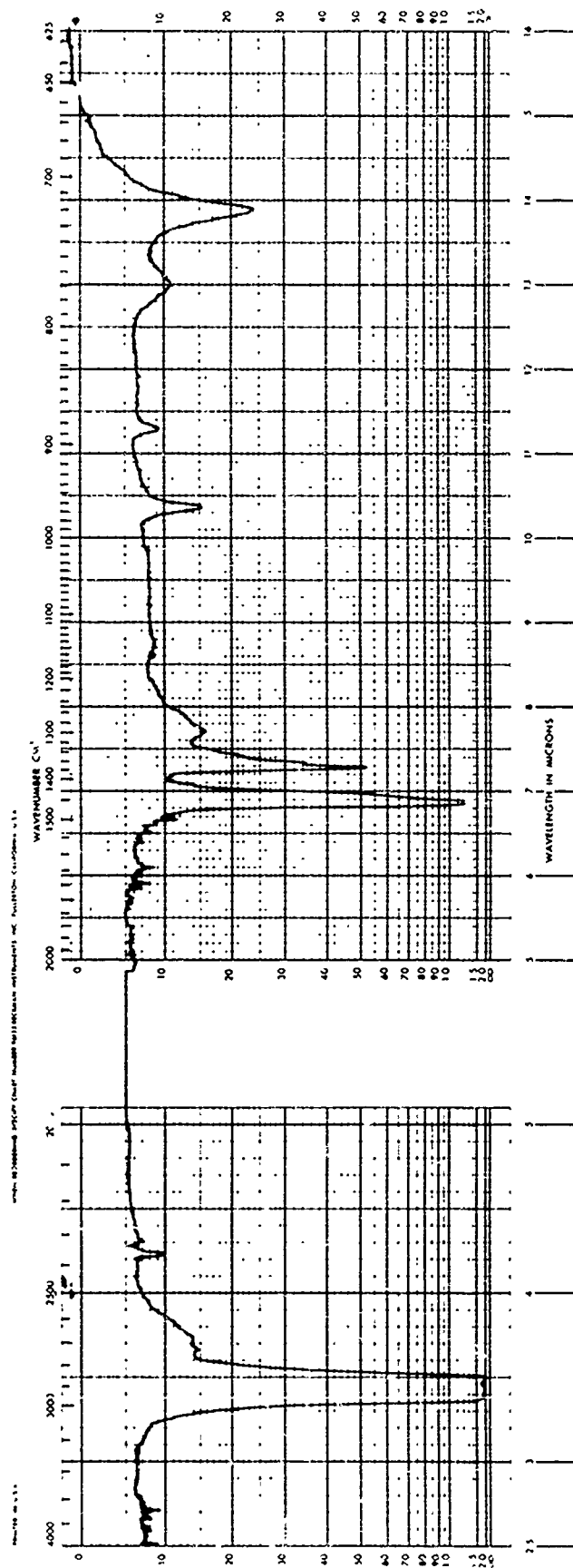


Figure 68 Infrared spectrum of nonfunctional OH-Telagen-S, fraction 369-71-I, capillary layer between NaCl plates.

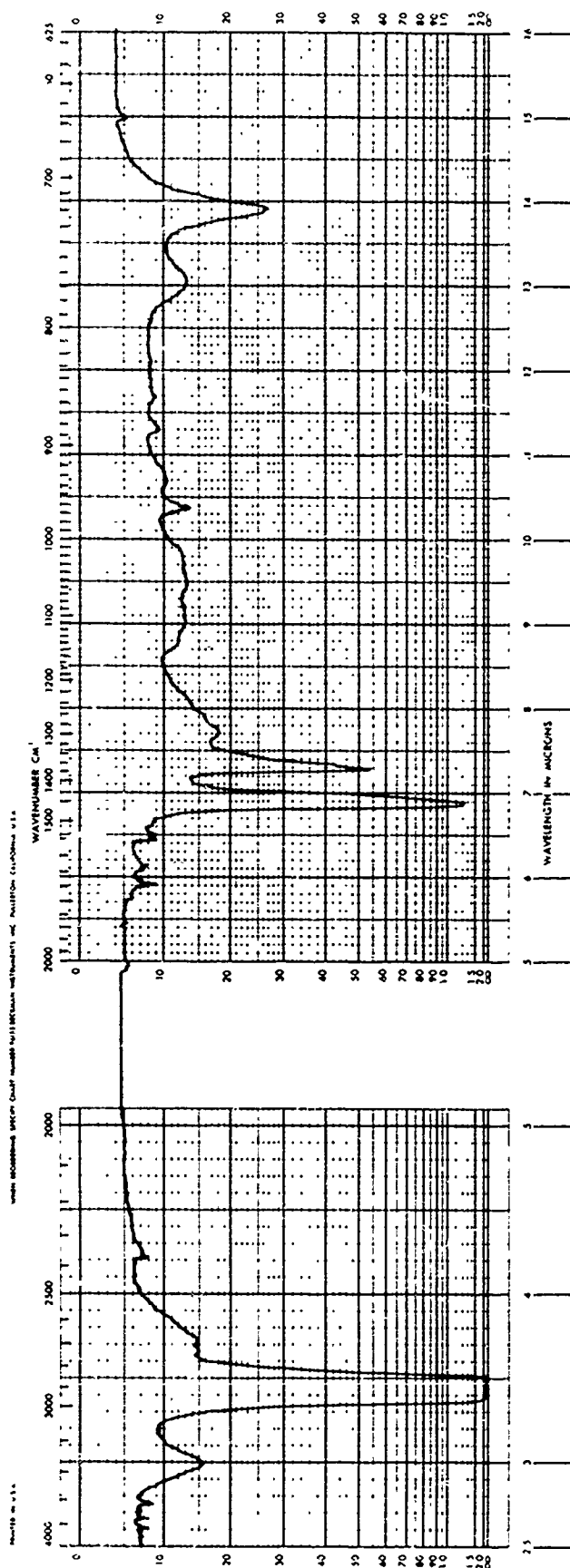


Figure 69. Infrared spectrum of monofunctional OH-Telagen-S, fraction 369-71-II, capillary layer between NaCl plates.

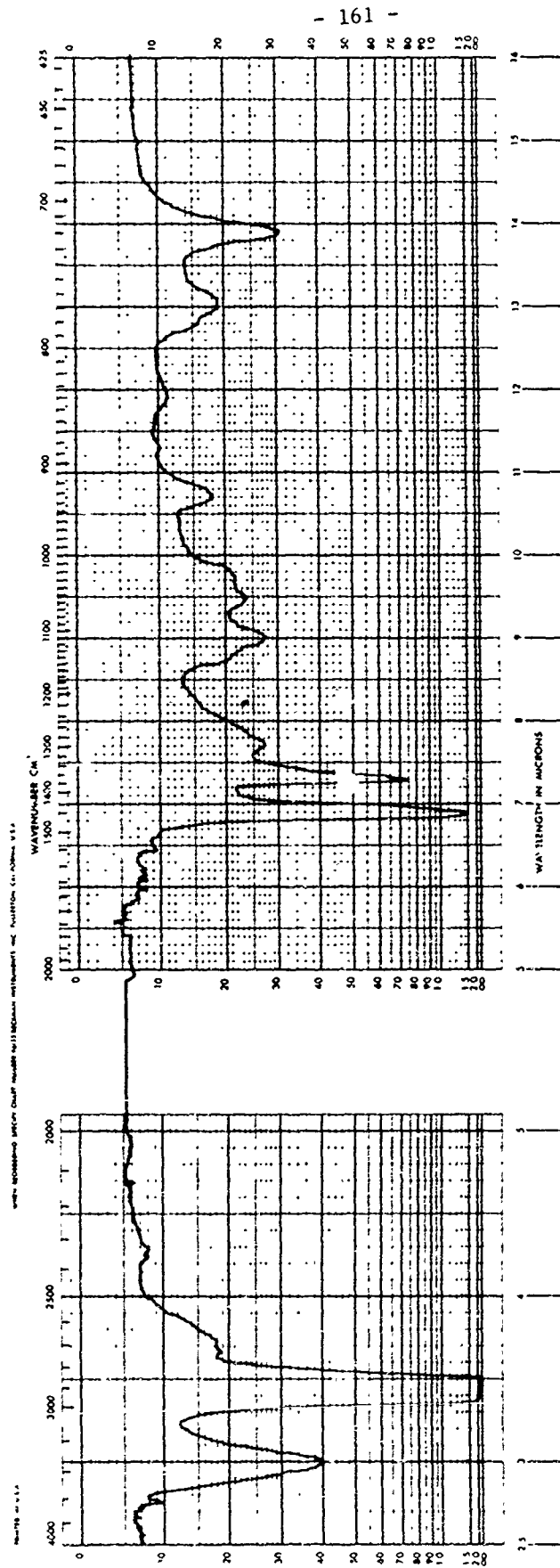


Figure 70. Infrared spectrum of difunctional OH-Telagen-S, fraction 369-71-IV, capillary layer between NaCl plates.

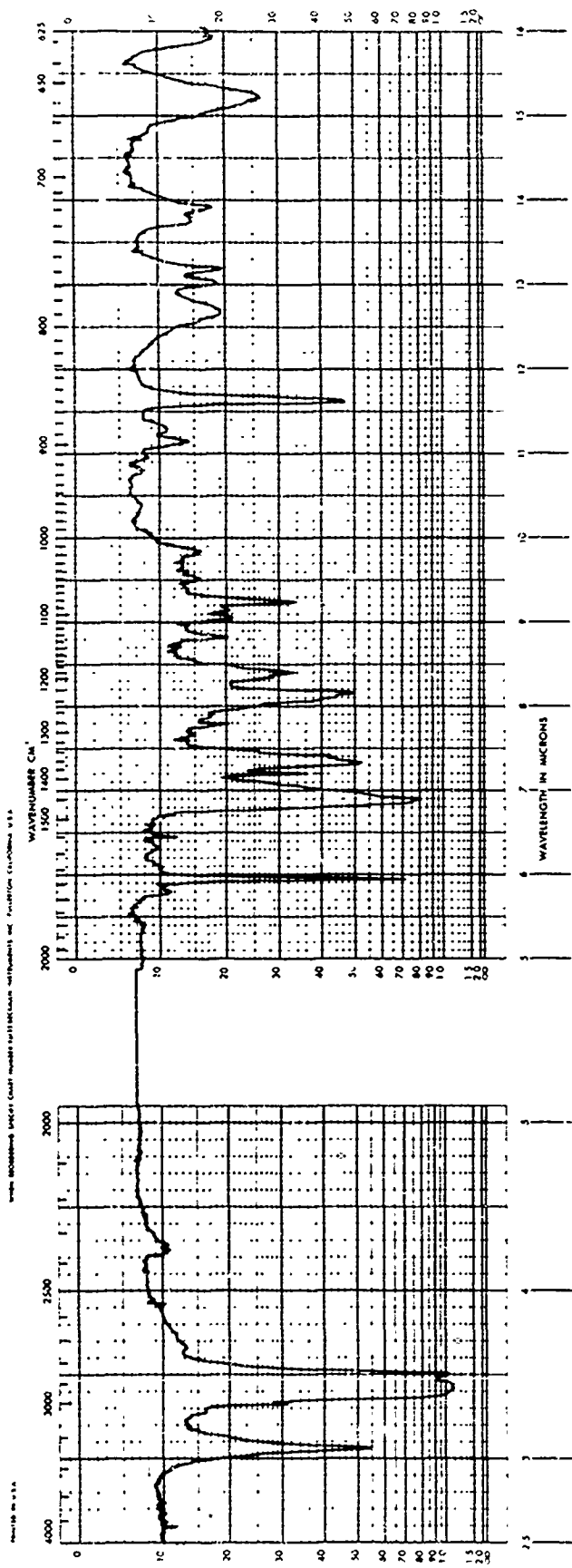


Figure 71. Infrared spectrum of OH-Telagen-S fraction 369-63-IV-S (sublimate), capillary layer between NaCl plates.

APPENDIX B-4

INFRARED SPECTRA OF COOH-POLYISOBUTYLENE FRACTIONS

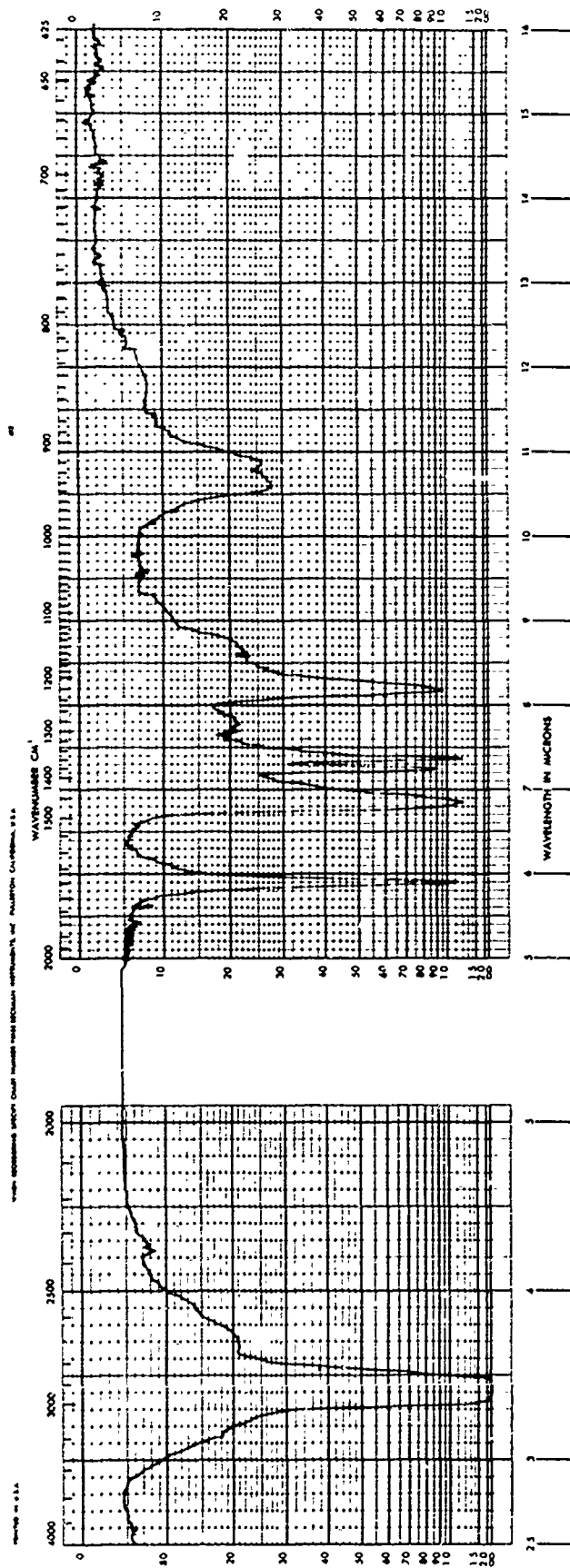


Figure 72. Infrared spectrum of COOH-terminated polyisobutylene, EMD-590, Lot CP₃ 21-1, whole polymer, capillary layer between NaCl plates

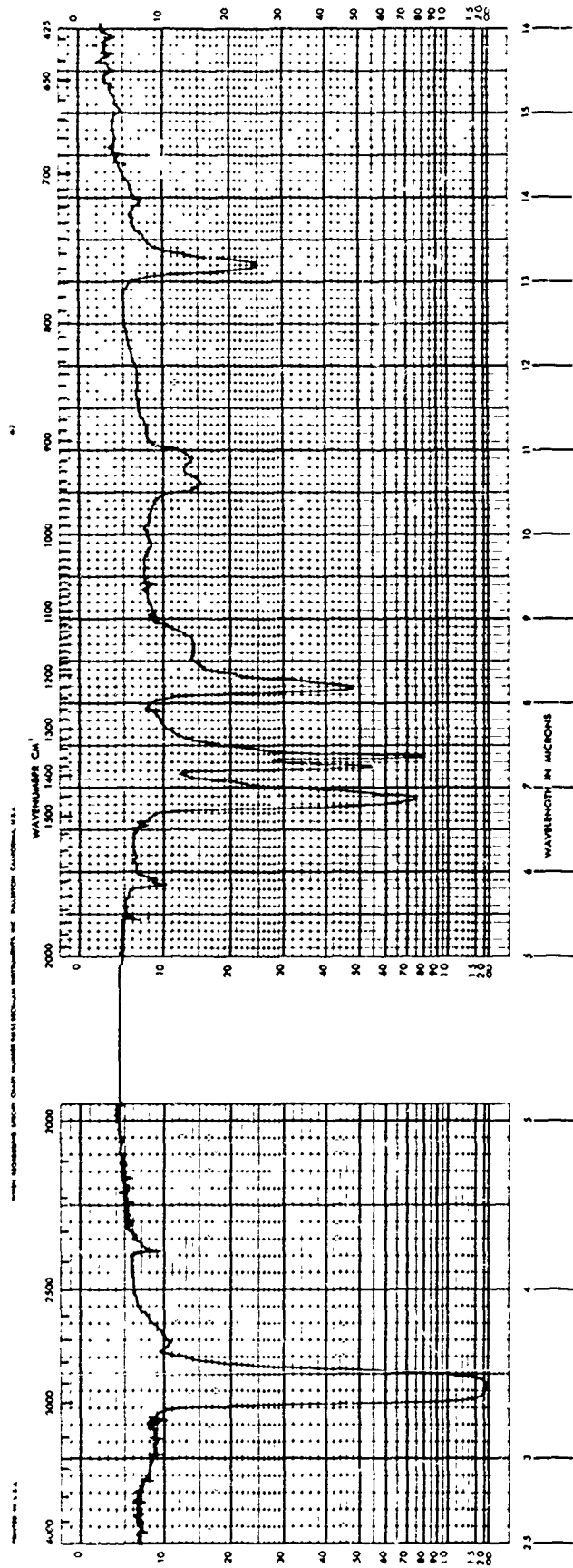


Figure 73. Infrared spectrum of essentially nonfunctional EMD-590, fraction 369-128-I, capillary layer between NaCl plates

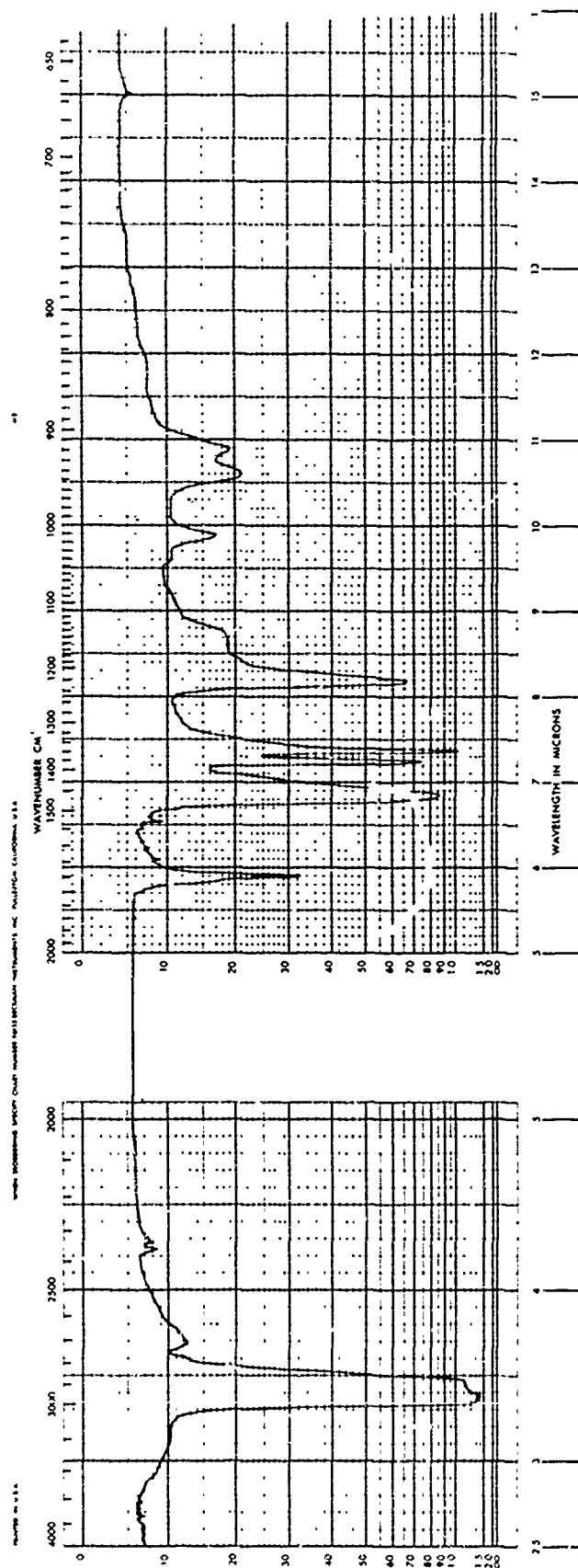


Figure 74. Infrared spectrum of monofunctional COOH-polyisobutylene, EMD-590, fraction 369-128-II, capillary layer between NaCl plates

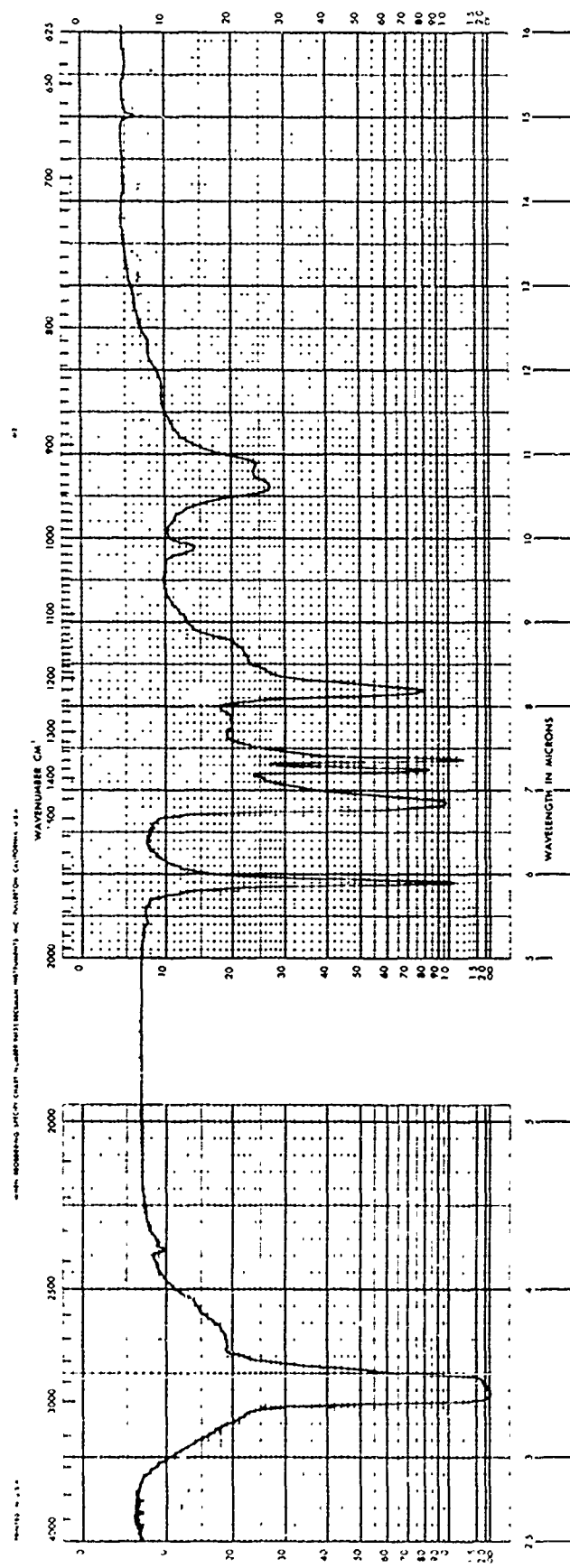


Figure 75. Infrared spectrum of difunctional COOH-polyisobutylene, EMD-590, fraction 369-128-III, capillary layer between NaCl plates

APPENDIX B-8

INFRARED SPECTRA OF CNR-NITROSO TERPOLYMER FRACTIONS

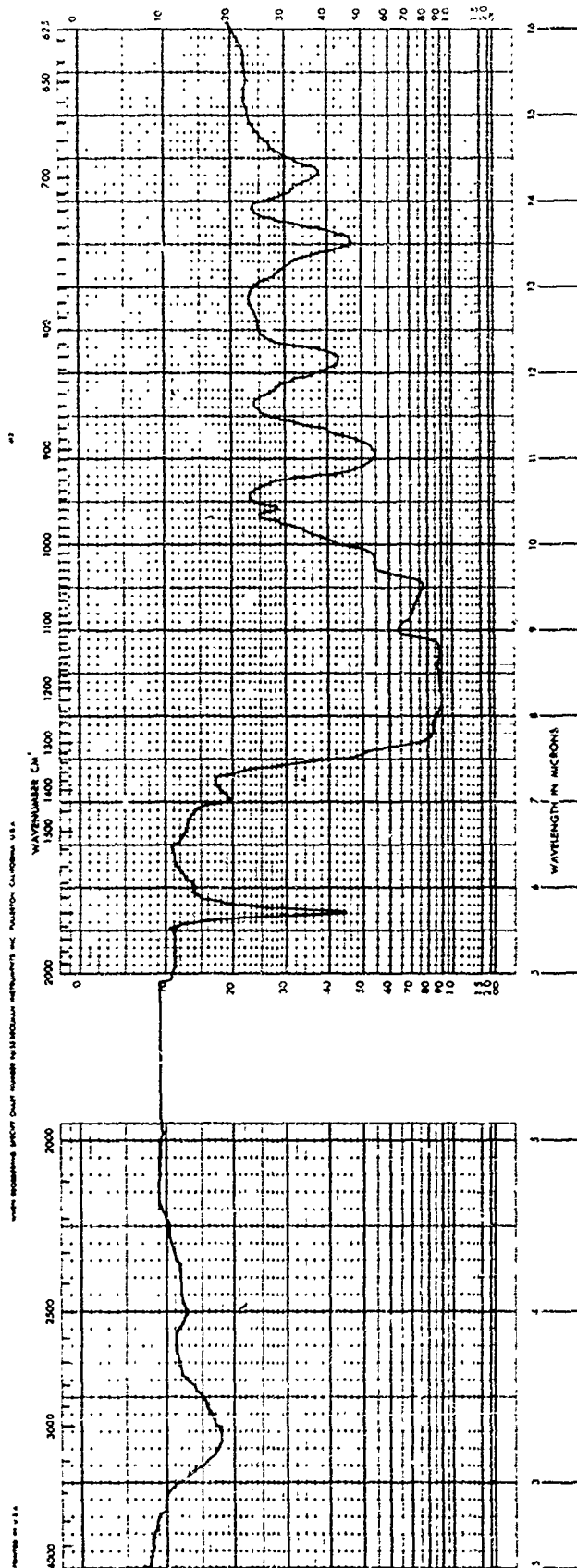


Figure 76. Infrared spectrum of CNR-nitroso prepolymer, Lot A001-4D, whole polymer, capillary layer between NaCl plates

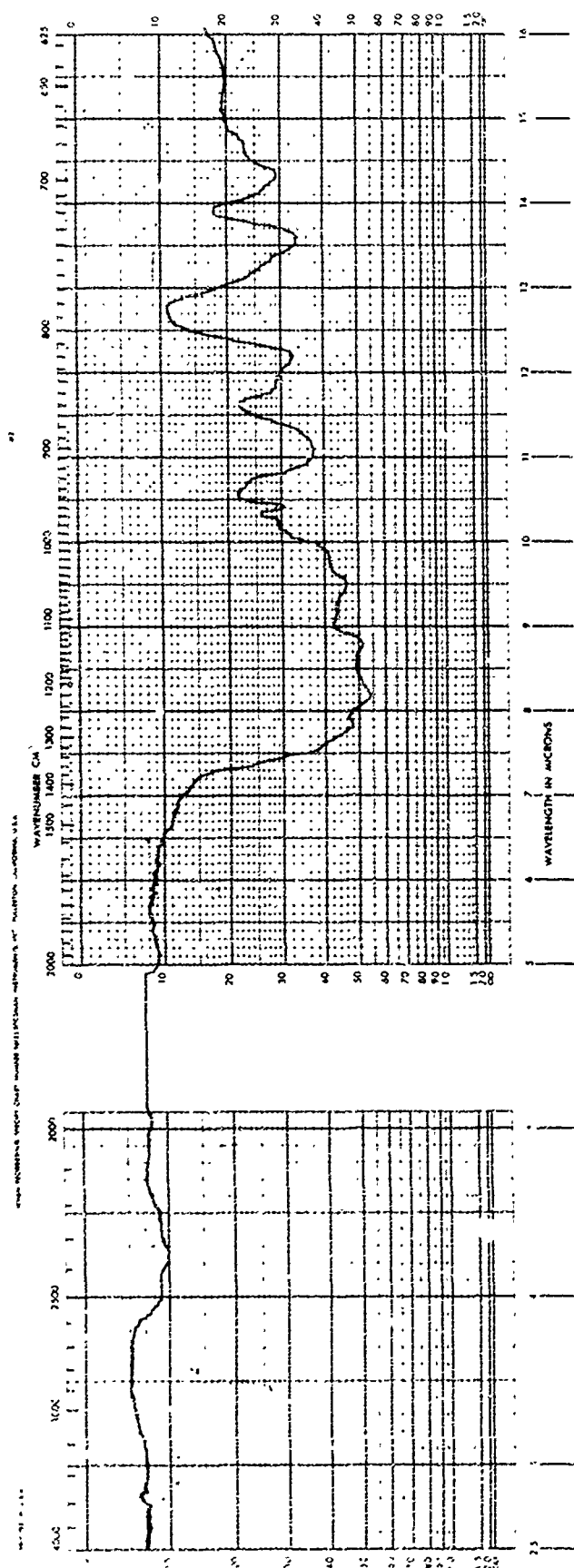


Figure 77. Infrared spectrum of nonfunctional CNR-nitroso prepolymer, capillary layer between NaCl plates.

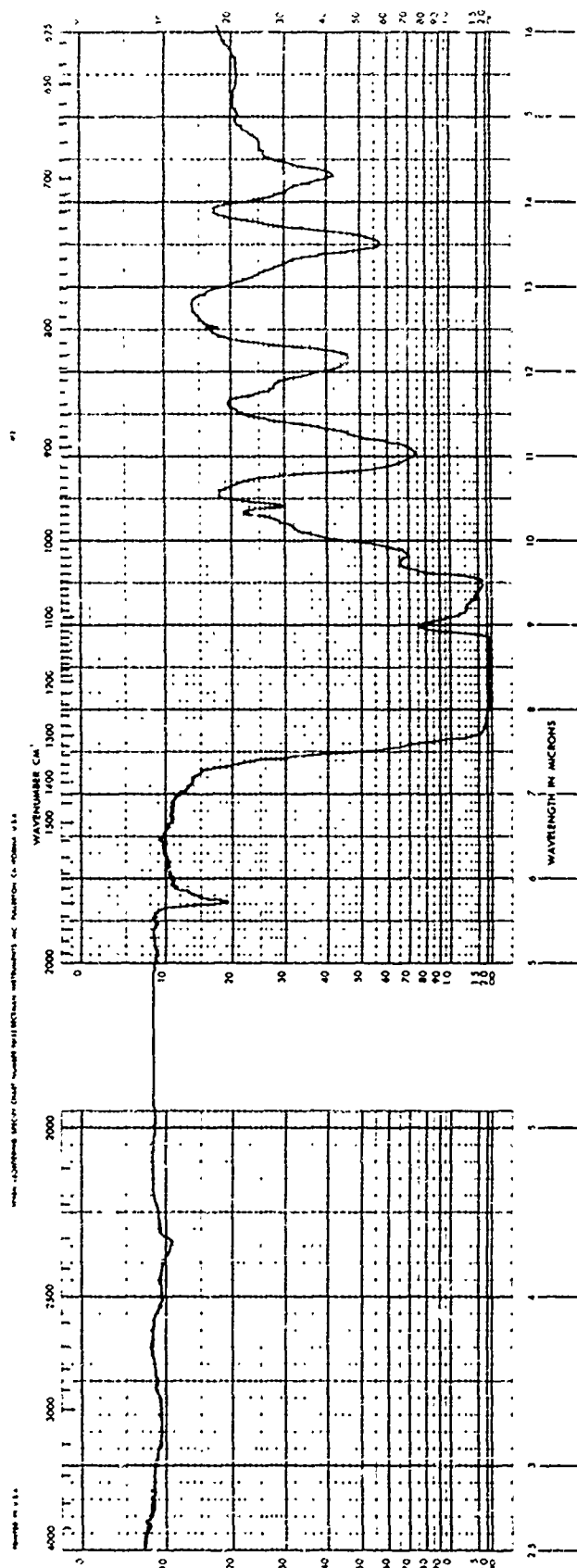


Figure 78. Infrared spectrum of CNR-nitroso polymer, fraction 369-156-I, capillary layer between NaCl plates. Fraction is an approximate 50/50% mixture of non- and monofunctional prepolymer

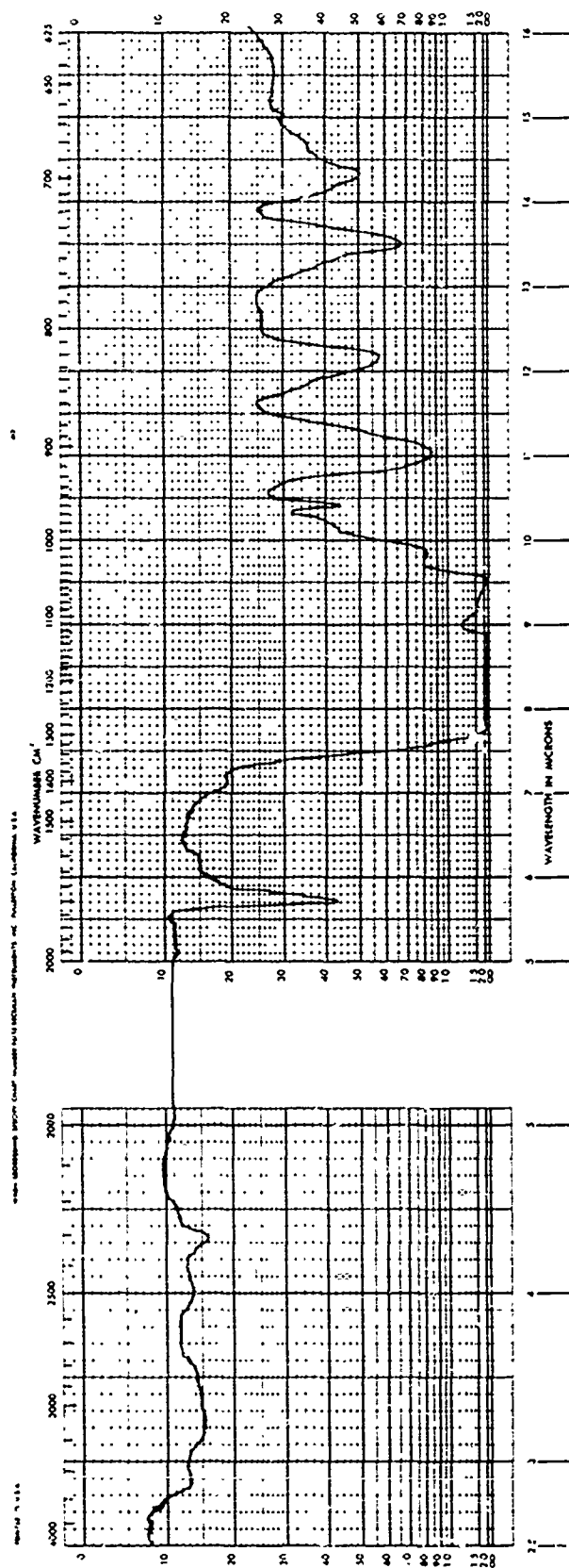


Figure 79. Infrared spectrum of CNR-nitroso prepolymer, fraction 369-156-II, capillary layer between NaCl plates. Fraction II is difunctional.

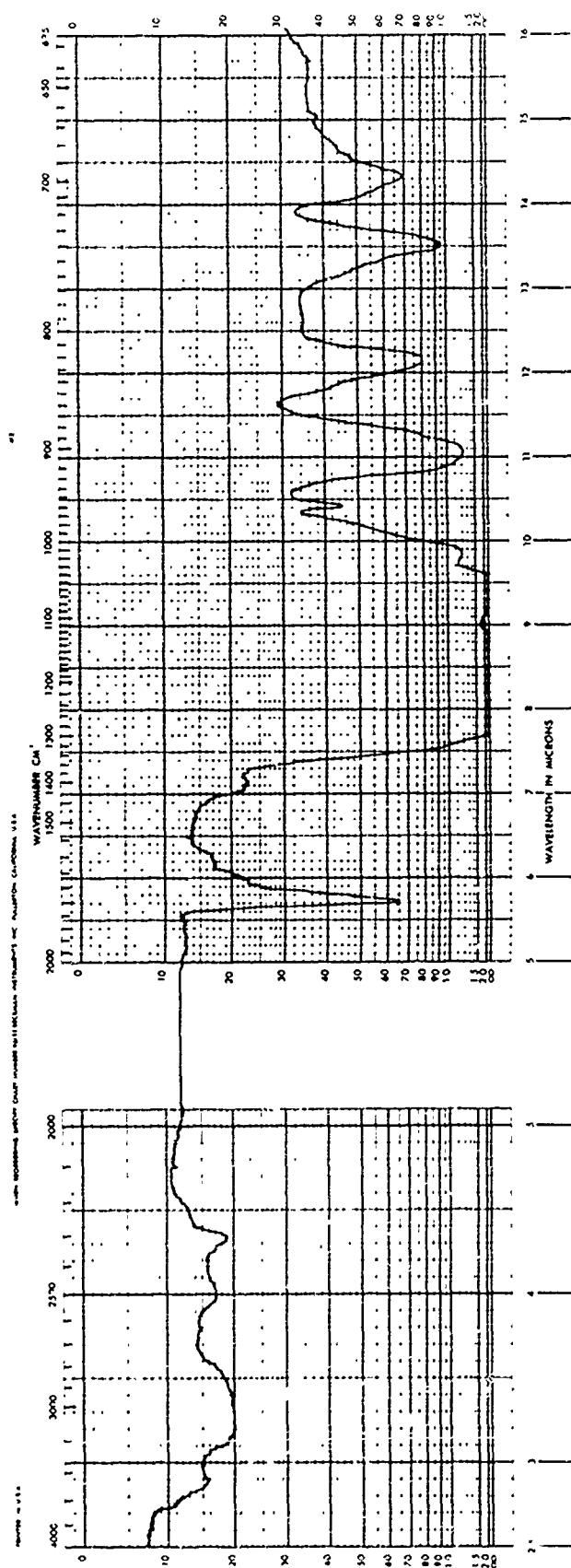


Figure 80. Infrared spectrum of CNR-nitroso prepolymer, fraction 369-156-III, capillary layer between NaCl plates. Fraction III is a mixture of tri- and tetrafunctional polymer

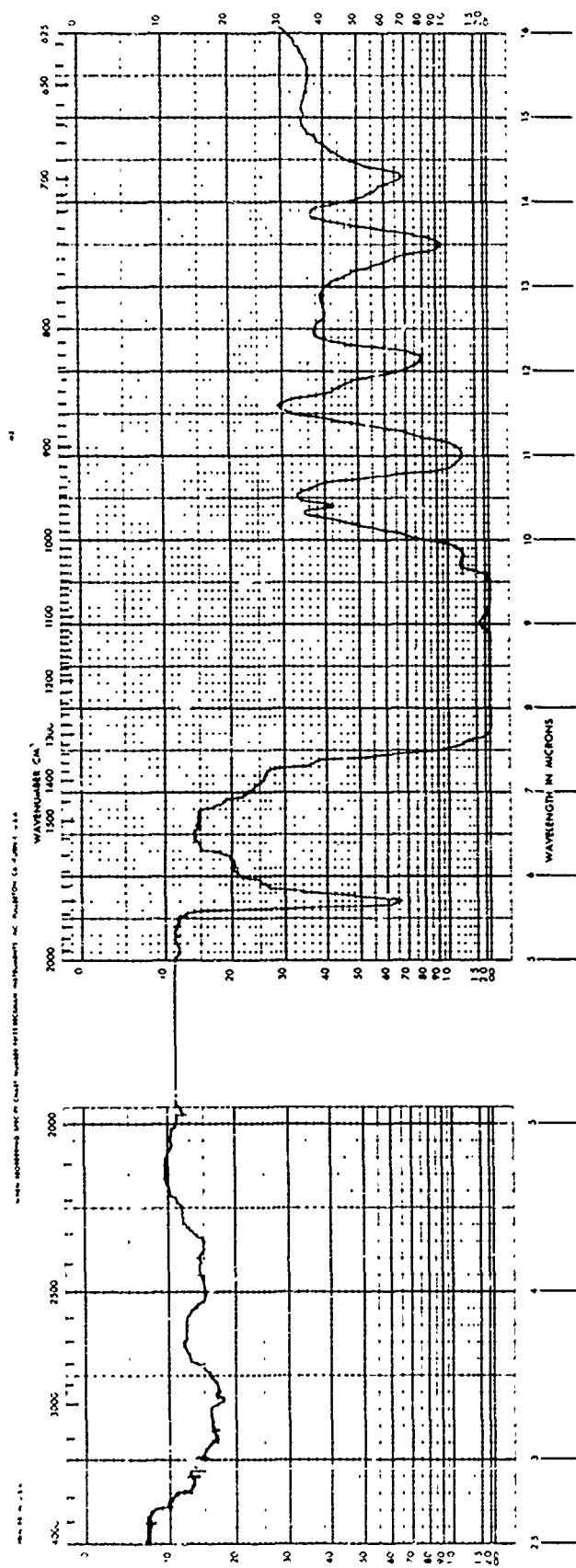


Figure 81. Infrared spectrum of CNR-nitroso prepolymer, fraction 369-156-IV, capillary layer between NaCl plates. Fraction IV is approximately pentafunctional.

APPENDIX B-9

INFRARED SPECTRA OF PERFLUOROALKYLENE OXIDE
PREPOLYMER FRACTIONS

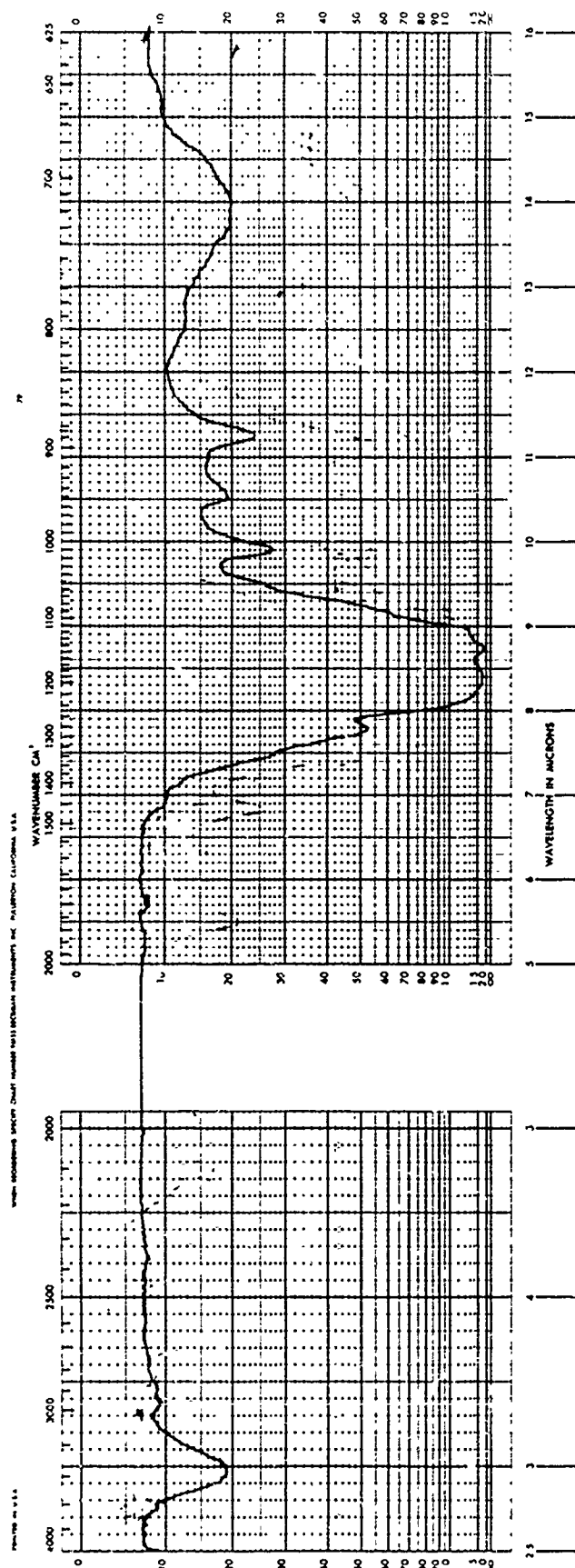


Figure 82. Infrared spectrum of 3M's hydroxy-functional perfluoroalkylene oxide prepolymer, whole polymer, capillary layer between NaCl plates.

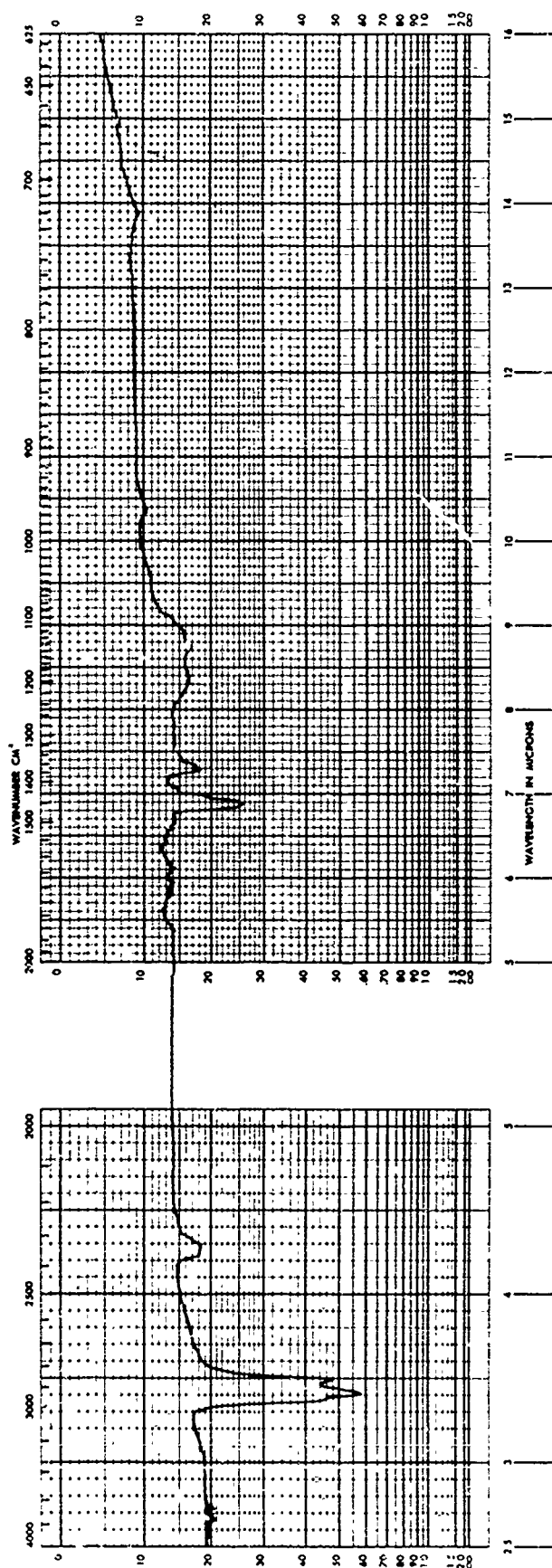


Figure 83. Infrared spectrum of polymer fraction 416-41-I, capillary layer between NaCl plates. Functionality = 1.08.

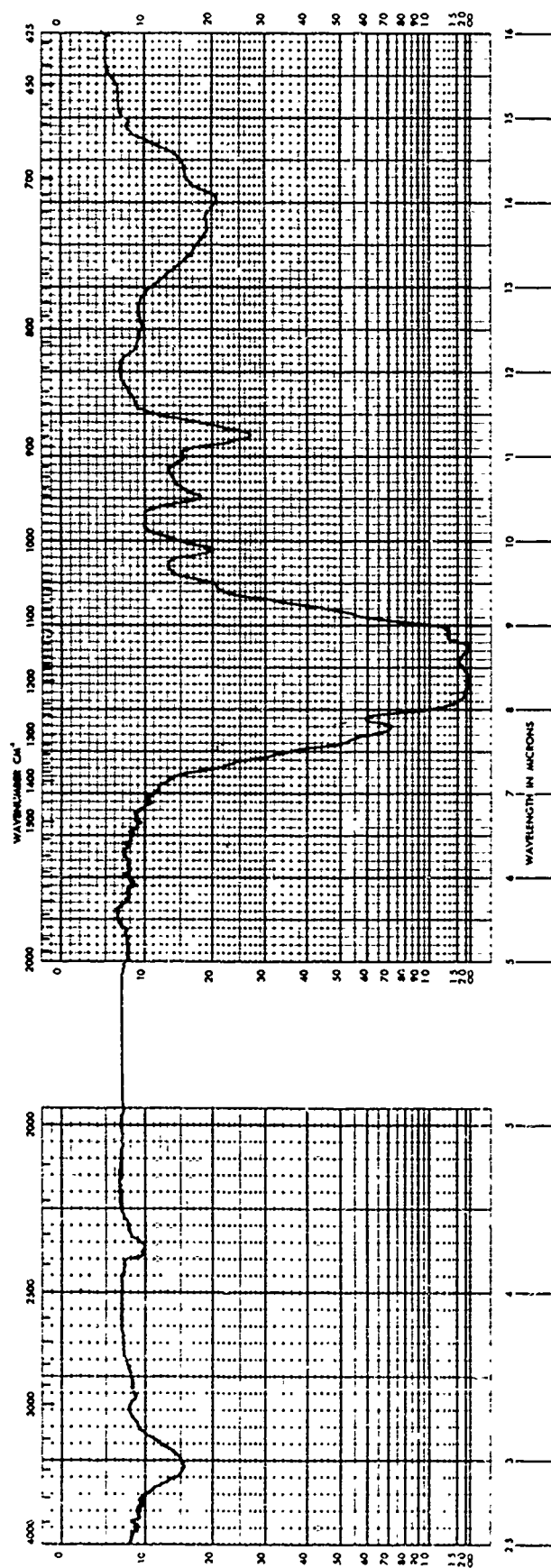


Figure 84. Infrared spectrum of polymer fraction 416-41-II, capillary layer between NaCl plates. Functionality = 2.26.

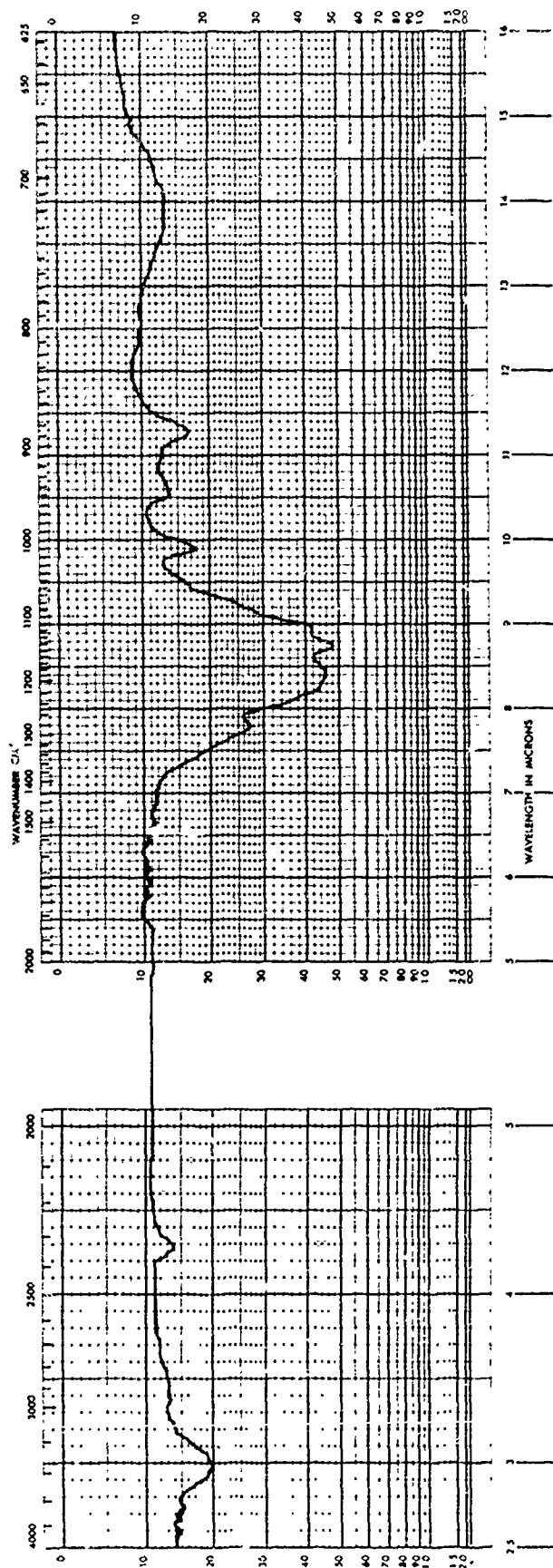


Figure 85. Infrared spectrum of polymer fraction 416-41-III, capillary layer between NaCl plates. Functionality = 2.26.

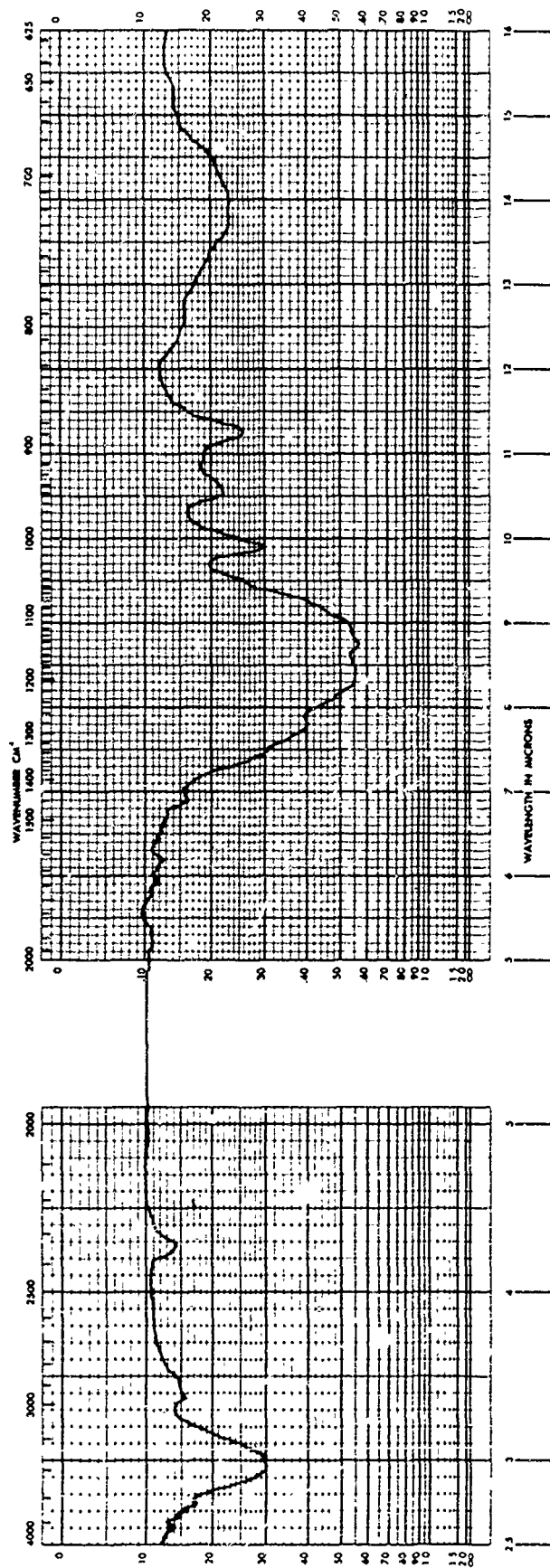


Figure 86. Infrared spectrum of polymer fraction 416-41-IV, capillary layer between NaCl plates. Functionality = 2.95.

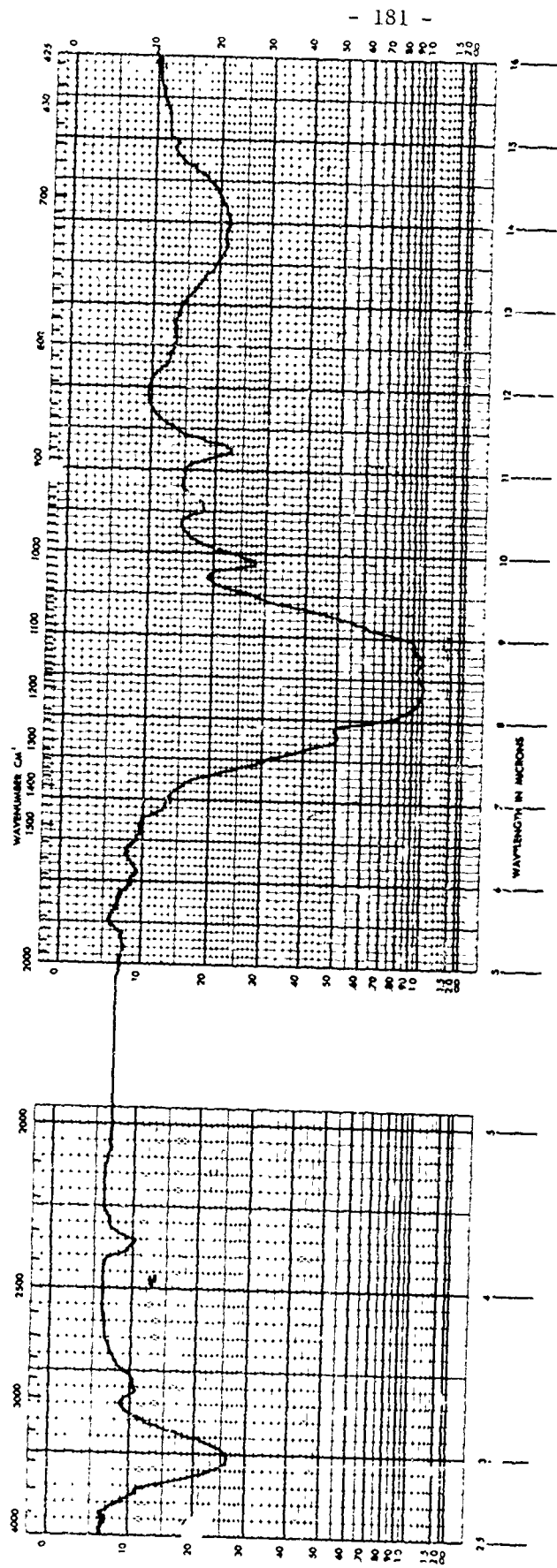


Figure 87. Infrared spectrum of polymer fraction 416-41-V, capillary layer between NaCl plates. Functionality ≈ 4.15 .

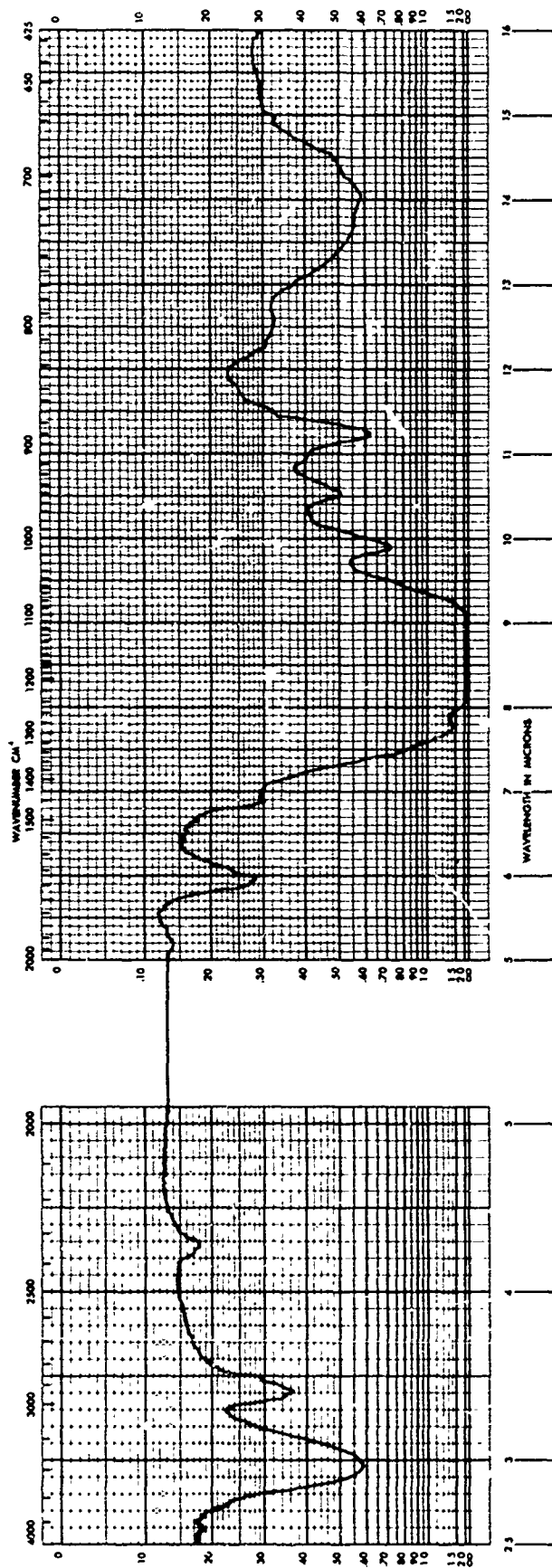


Figure 88. Infrared spectrum of polymer fraction 416-41-VI, capillary layer between NaCl plates. Functionality = 3.76.

APPENDIX B-10

INFRARED SPECTRA OF
COOH-BUTAREZ FRACTIONS

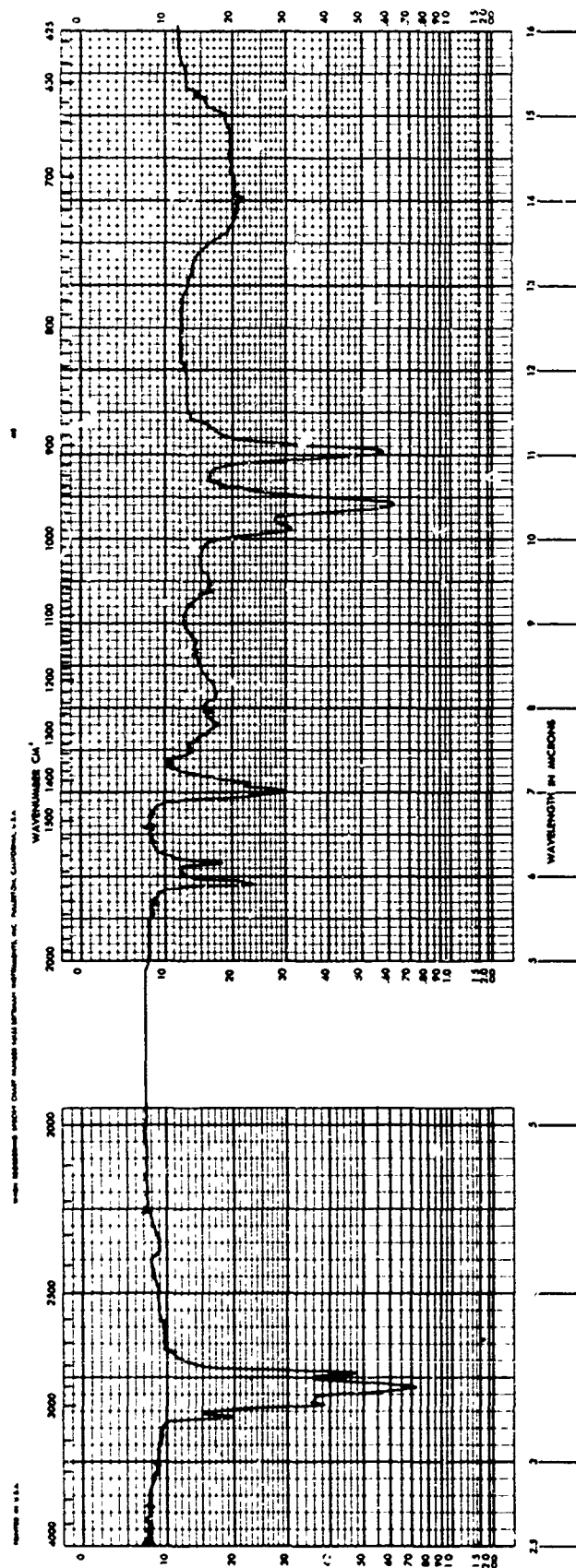


Figure 89. Infrared spectrum of COOH-Butarez, Type II, lot 2285, whole polymer, capillary layer between NaCl plates.

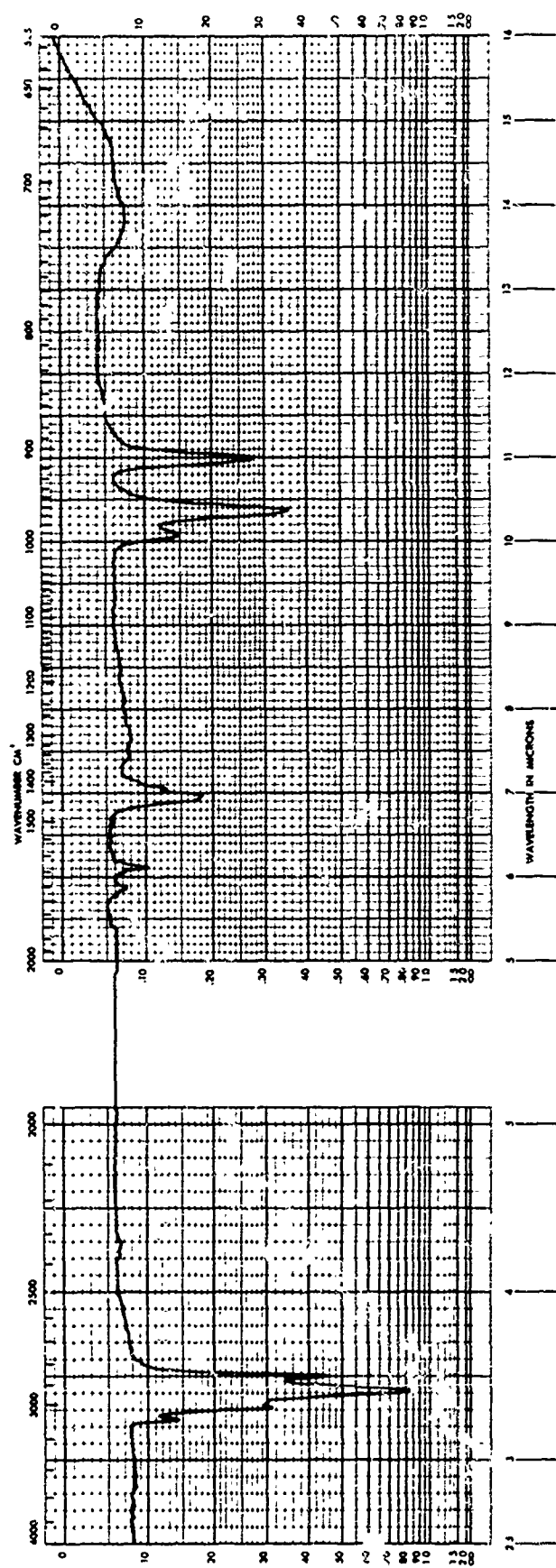


Figure 90. Infrared spectrum of Butarez, fraction 416-15-I, capillary layer between NaCl plates; functionality = 0.34.

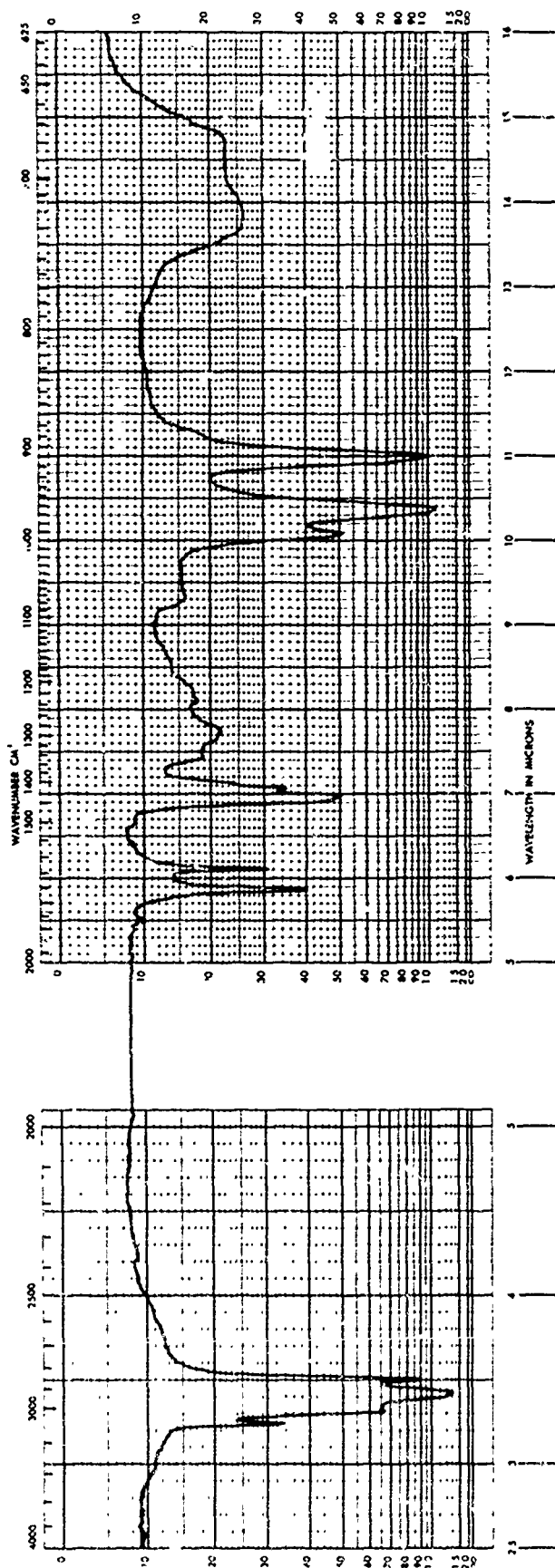


Figure 91. Infrared spectrum of Butarez, fraction 416-15-II, capillary layer between NaCl plates; functionality = 1.68.

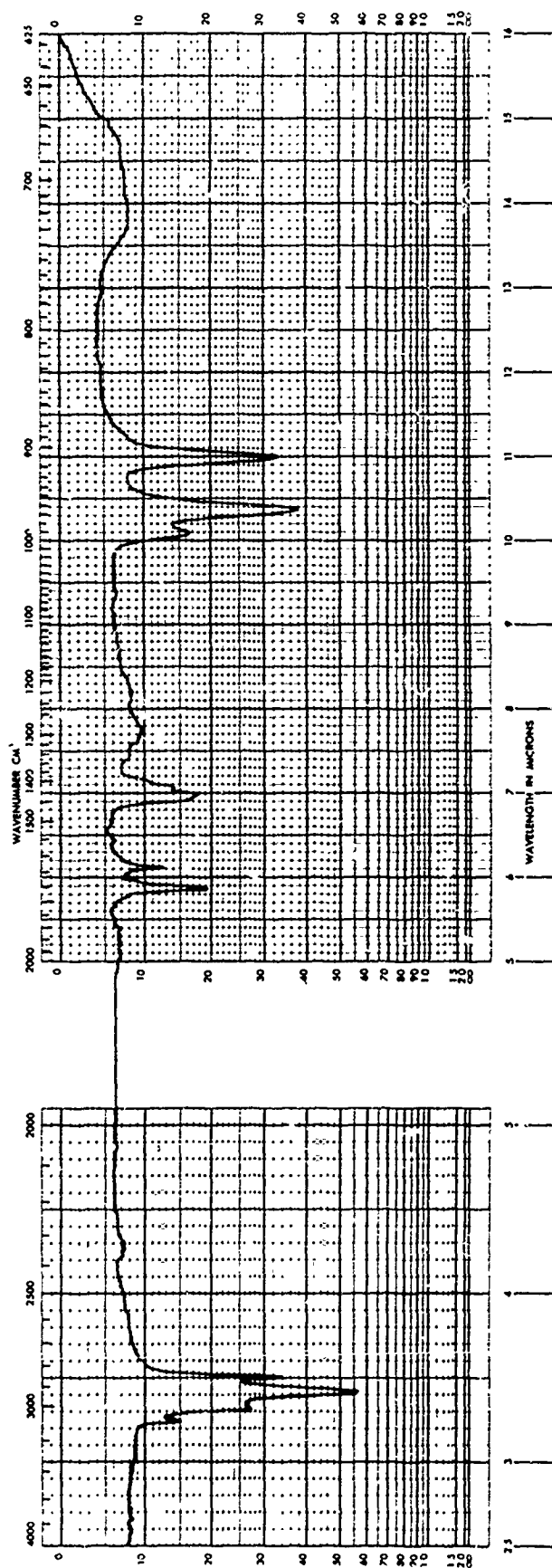


Figure 92. Infrared spectrum of Butarez, fraction 416-15-III, capillary layer between NaCl plates: functionality = 2.53

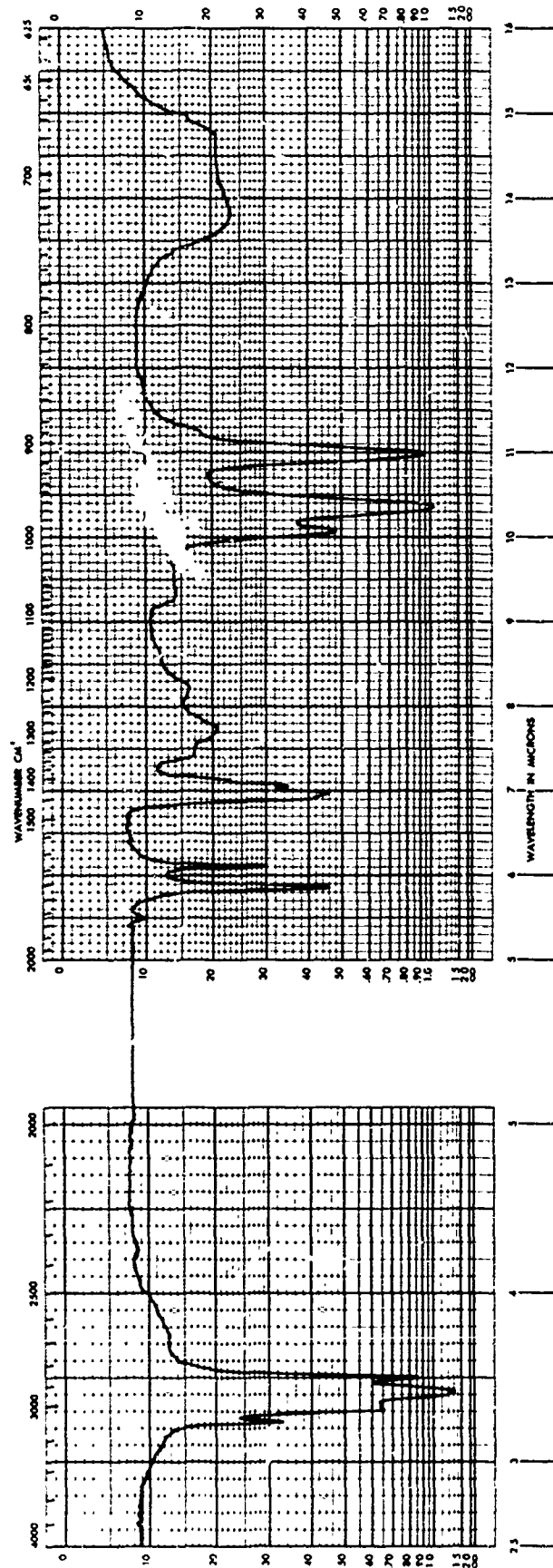


Figure 93. Infrared spectrum of Butarez, fraction 415-15-IV, capillary layer between NaCl plates; functionality = 2.45

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<p>✓ This is the final report describing research aimed at the development of accurate and reasonably fast procedures to determine the functionality and functionality distribution of prepolymers currently of interest to the Air Force. Research was carried out under Contract No. F04611-67-C-0012 during the period October 1, 1966 to September 30, 1968. ✓ The effect of solute concentration, solvent type and temperature on number average molecular weight measurements by VPO was studied for a series of binder prepolymers. It was concluded that molecular weight measurements of a given polymer in different solvents give identical molecular weights when extrapolated to infinite dilution, although measurements at finite concentrations in different solvents may give widely varying results. ✓ A number of micro-methods were developed which can accurately determine the equivalent weight of hydroxy- and carboxy-functional prepolymers on a 50 to 100 mg sample size. A method was also developed to determine the functionality distribution of binder prepolymers. The method is based on the adsorption of prepolymer on activated silica gel and subsequent selective desorption by stepwise elution using solvent mixtures of progressively greater elution power. The following eight prepolymers were characterized on this program: OH-Telagen-S, COOH-Telagen-S, P-BEP, 3M's hydroxy-functional perfluoroalkylene oxide prepolymer, COOH-Polyisobutylene, Thiokol's CNR-Nitroso Terpolymer, COOH-Butarez and Sinclair's Poly B-D. Typical prepolymer samples contain from 0-7% nonfunctional polymer, and 16 to 33% monofunctional polymer.</p>		

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